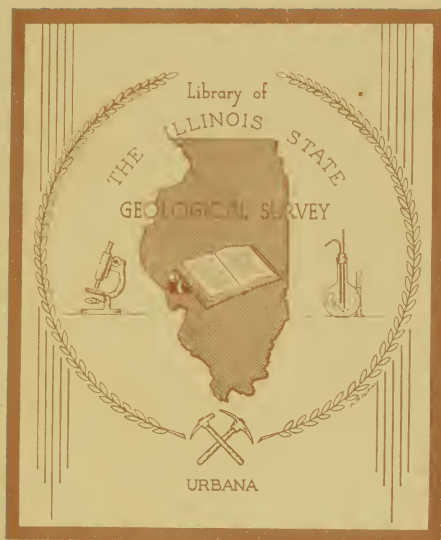



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BULLETIN No. 18

A Study of Sand-Lime Brick

BY

S. W. PARR

AND

T. R. ERNEST



Urbana
University of Illinois
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LETTER OF TRANSMITTAL.

STATE GEOLOGICAL SURVEY,
UNIVERSITY OF ILLINOIS, Feb. 7, 1912.

Governor C. S. Deneen, Chairman, and Members of the Geological Commission:

GENTLEMEN—I submit herewith manuscript for a report entitled, A study of sand-lime brick, and recommend that it be published as Bulletin No. 18. The report was prepared by Prof. S. W. Parr, consulting chemist of the Survey, in collaboration with Dr. T. R. Ernest.

No sand-lime bricks are now produced in Illinois, though the industry has a footing in neighboring states, and, if we may judge from foreign experience, will become prominent here in the future.

Very respectfully,

FRANK W. DEWOLF,
Director.

PREFACE.

The finely divided silica occurring in numerous deposits in southern Illinois has for some time been the subject of study in the Laboratory of Applied Chemistry in the University of Illinois. Investigations upon this material were begun in the year 1905 by Mr. C. F. Hagedorn, and have been continued by Messrs. C. M. McClure, W. S. Williams,¹ and A. W. Beemer. The purpose of this work was to determine the possibility and extent of a reaction which might be brought about between the silica and lime by means of steam pressure, somewhat after the manner of the practice followed in the manufacture of sand-lime bricks. The extent of the deposits made it appear probable that this material might find an application in the manufacture of some such ceramic product as wall or floor tile, architectural decorative material, or as a filler in sand-lime bricks.

The possible use of the silica in the manufacture of sand-lime brick suggested the advisability of a study of the sand-lime brick process from both a theoretical and a practical standpoint, in order to determine the effect of substituting the silica for some of the sand commonly used in the process. It seemed desirable to investigate very closely the chemical and physical properties of compounds formed from finely divided silica and lime, inasmuch as these are evidently very closely related to the bonding material in sand-lime brick, if, indeed, they are not identical with it. It had been determined by the earlier experiments that when mixed with lime, this silica enters into a reaction which results in the production of a homogeneous compound. This new substance, it was assumed, must resemble the film of hydrated calcium silicate surrounding the sand grains in sand-lime bricks.

That good bricks can be made from sand and lime is no longer questioned. The matter of cost of their manufacture, however, should be carefully determined for any locality at which it is proposed to erect a plant, in order to avoid the mistake of building in a situation where the manufacture of the bricks is not economically practicable.

Illinois is no longer represented in the list of states producing sand-lime bricks, although there are in it, doubtless, many localities in which their manufacture would be profitable both to the producer and to the consumer. It seems fitting, therefore, that some information relative to this industry should be published by the State Geological Survey. It is the purpose of this bulletin to discuss briefly the chemistry of sand-

¹ Bull. Ill. State Geol. Survey, No. 14, 1909, p. 275.

lime bricks and the conditions that are most favorable for the production of bricks of good quality. Incidentally, the results of several series of tests on commercial bricks are given.

In the preparation of this bulletin the authors wish to acknowledge gratefully the services rendered them by the Anderson Foundry and Machine Company in the use of their experimental plant for the manufacture of sand-lime bricks; to Mr. R. T. Stull, of the Department of Ceramics of the University of Illinois, for the use of kiln and accessories in fire tests; to Prof. A. N. Talbot, Mr. D. A. Abrams, and Mr. A. R. Lord, of the Laboratory of Applied Mechanics of the University of Illinois, for assistance given in testing, and for the use of the facilities of the laboratory; to Prof. W. S. Bayley, for valuable suggestions in the use of the polarizing microscope; to the United States Brick Corporation and the Excelsior Brick Company, of Michigan City, Indiana, for samples of bricks used in some of the tests, and to Mr. E. B. Stephenson, of the Chemical Laboratory of the University of Illinois, for assistance in making photomicrographs.



House built of mortar brick in 1872.

HISTORICAL INTRODUCTION

The manufacture of building bricks from mixtures of sand and lime began more than half a century ago, but the modern methods of manufacture are of much more recent origin. The first bricks prepared from sand and lime have been properly called "mortar bricks," for in reality they consisted of nothing more than common lime mortar molded into bricks and allowed to harden by the absorption of carbonic acid from the atmosphere. In this process it was necessary to use enough lime to surround the sand grains and give a more or less plastic mortar which could be molded in a manner similar to the soft-mud process for making clay brick. The amount of lime used varied from 20 to 40 per cent, depending on its quality. The hardening was due to the formation of calcium carbonate, and, when finished, the bricks consisted of grains of sand embedded in a sort of artificial limestone. There was no appreciable union of the sand grains chemically, but they were held in place by a network of calcium carbonate; or, if very much lime was used, it is perhaps more exact to speak of the sand particles as being embedded in a mass of calcium carbonate. The sand served the purpose of preventing the brick from shrinking on drying, and at the same time, it reduced the amount of lime required in the mixture, just as the rock, sand, and other fragmental material in concrete, reduce the amount of cement required in it.

The objections to "mortar bricks" are obvious, and it is not surprising that the bricks were used only in regions where the soil was sandy, and clays for making other kinds of bricks could not be found. Moreover, the large percentage of lime required in their manufacture and the long time necessary for hardening them, especially in wet seasons, made them too costly to compete with common bricks. Notwithstanding these difficulties, however, bricks made by the mortar process possessed wonderful strength and durability. Plate I is the picture of a building erected half a century ago in which material of this character was used.¹ It illustrates the remarkable durability of properly made "mortar bricks."

In order to hasten the hardening of the mortar bricks it became the practice to store them in enclosed sheds and to enrich the atmosphere

¹ The present occupant of the house says: "For your information, will say that it is a two-story house built of sand-lime brick, 4 by 5 by 10 inches, in 1872. Not a brick in the entire building has shown the least deterioration up to the present time."

with carbonic acid. Afterward, steam and carbonic acid were delivered into the curing sheds and the time required for hardening was thereby further shortened. This latter procedure resulted in the formation of a bond composed of both calcium carbonate and hydrated calcium silicate, thus yielding bricks superior to those produced by the original process in which the bond was exclusively carbonate.

In 1881 Dr. W. Michaelis took out a patent (D. R. P. Nr. 14195) for hardening mixtures of lime and sand by high pressure steam. This is briefly described as follows: "High pressure steam is allowed to act for a number of hours upon a mixture of 10 to 40 parts lime (or barium or strontium hydrate) with 100 parts sand (or minerals containing silicic acid) at a temperature from 130° to 300° C., in a specially constructed apparatus. There results a silicate which forms a hard, air-and-water-resisting mass." The patent lapsed before any commercial use had been made of it. Like many other inventions, this one probably failed to be of value because of a lack of development in some related industry. For instance, it was not until the engineer and chemist had improved the methods of steel manufacture so that cylinders in which the bricks are hardened could be constructed of sufficient strength to bear the burden, that the manufacture of the bricks was possible on a commercial scale.

In 1896 there were in Germany several plants in operation using the process patented by Dr. Michaelis, but it was not until the year 1898 that sand-lime bricks were produced on a large scale even in that country. From this date, however, to the present time the industry has there enjoyed a healthy growth. In the beginning of July, 1908, there were 285 German sand-lime brick plants, producing from 900 to 1300 million sand-lime bricks annually. As is usually the case with new materials of construction, considerable trouble was experienced in marketing the product. There was at first a great deal of prejudice against the new bricks on the part of architects and contractors, and perhaps justly so, but this has now almost completely disappeared. The new material has won favor with the German Government, so that now in government work sand-lime bricks are not only tolerated but actually specified in many cases. The *Verin der Kalksandsteinfabriken* has done much to remove this prejudice by disseminating information, making tests, standardizing specifications, etc. The industry is well enough advanced in Germany to support a publication devoted to its interests.

Other countries soon followed the example of Germany. In the United States the first plant, that of the Olemacher Brick Company, was built in Michigan City, Indiana, in the year 1901; and in 1902 there were five factories in operation, with a total daily output of about 100,000 bricks. It is reported that the sales during this year were 6,000,000 bricks. The first reliable statistics of the sand-lime brick industry were collected by the United States Geological Survey for the year 1903. Succeeding years show a very rapid increase in the number of bricks made, until the year 1907, when, of course, all industry was

checked owing to the financial condition of the country. The following table will show the production in the United States, as reported by the Geological Survey.¹

TABLE 1—*Production of sand-lime brick in the United States.*

Year.	Number of plants.	Value of product.	Prices per M.		
			Common.	Face.	Fancy.
1901.....	1				
1902.....	5				
1903.....	16	\$ 155,040			
1904.....	57	463,128			
1905.....	84	973,064			
1906.....	87	1,170,005	\$6 71	\$10 42	
1907.....	94	1,225,769	6 61	10 96	
1908.....	87	953,552	6 33	12 16	\$25 66
1909.....	74	1,046,184	6 39	11 98	27 13

The development of the industry in this country has been very satisfactory. There are, however, some localities in which the manufacturer finds difficulty in marketing his product, because of prejudice on the part of architects. The American industry is greatly in need of more publicity, but this publicity should be of the right kind, and free from exaggerations such as are to be found in the advertising literature of some promoters. There is an organization of the manufacturers of sand-lime bricks which is known as The American Sand-Lime Brick Manufacturers' Association, which will doubtless perform a work corresponding to that of the Kalksandsteinfabriken of Germany. A good publication devoted to the industry is very greatly needed, and it is to be hoped that one will soon be established, in order that the literature relating to all phases of the sand-lime brick manufacture may be available in a single publication.

¹ Middleton, Jefferson: Mineral Resources U. S. for 1909, U. S. Geological Survey, 1911, p. 551.

GENERAL CONSIDERATION OF THE SAND-LIME BRICK INDUSTRY.

MEANING OF THE TERM "SAND-LIME BRICK."

Sand-lime brick or the "Kalksandstein" of the Germans, may be defined as a mass of sand grains cemented together by hydrated calcium silicate. If the lime used in the manufacture is dolomitic there will be in the bond hydrated magnesium silicate as well as calcium silicate, but experience has shown that the best product is obtained when the percentage of magnesium oxide in the lime is low. The reaction between lime and silica resulting in the formation of hydrated lime silicates takes place slowly at ordinary temperatures in moist atmospheres, but in practice it is hastened by the action of steam. Sand-lime brick differs from sandstone, mortar, and silica brick primarily in the nature of the bond.

Sandstone is formed from beds of sand which have been laid down and covered by later strata. The sand is first closely packed by the pressure of the strata above. The cementation, or formation of bond, then begins, and is effected by the deposition, in the interstices between the sand grains, of various chemical substances that may be carried in solution by percolating water. Such substances are calcium, magnesium, and iron carbonates; calcium, barium and strontium sulphates; etc. The bond in the sandstone is purely a mechanical one, and the stone possesses its strength, its power of resistance to frost, heat, etc., by virtue of its compactness.

In the case of mortar, mortar brick, etc., the sand and one constituent of the bonding material are incorporated at the time of preparation of the mixture. In order that the mass may harden, it is necessary that another constituent, viz: carbonic acid, be added to change the soluble calcium hydroxide into the insoluble carbonate. This is obtained from the atmosphere. The bond in this case is almost entirely mechanical, as it is in the case of natural sandstone.

Hydraulic mortars differ from ordinary lime mortars in that they are capable of hardening without the addition of carbonic acid. The bond in this mortar consists of silicates and aluminates of calcium and magnesium, but there is no appreciable chemical reaction taking place between the silica of the sand and any of the bonding constituents. The bond in this case is mechanical, as before.

The material of silica bricks resembles that of sand-lime bricks more closely, perhaps, than does any other material. Silica bricks are made quite extensively for use as refractory linings for furnaces. They consist of sand grains cemented together by true calcium silicate. They are prepared by mixing lime and silica in the proportion of about 3-4 per cent of the former to 96-97 per cent of the latter, subjecting to great pressure in molding, and burning at a rather high temperature. The lime reacts with the silica of the sand forming a kind of glass which cements the sand grains together. The difference between a silica brick and the common sand-lime brick is that in the former little lime is used, and the hardening is done by firing in a kiln; while sand-lime bricks contain much more lime and they are hardened by the action of saturated steam under pressure. In silica bricks the bond consists of a glass containing no water; while in the case of sand-lime bricks, the bond is not a glass but a hydrated silicate, very much akin, no doubt, to some of the constituents of set Portland cement.

THE CONSTITUENTS OF SAND-LIME BRICKS.

Exclusive of the impurities always found in the raw materials of sand-lime bricks, their primary constituents are silica (SiO_2), lime (CaO), and water (H_2O). Inasmuch as any industrial process can be only imperfectly understood without a knowledge of the chemistry of the materials used in the process, it seems well to discuss briefly, at this point, the chemistry of silica and lime.

THE ELEMENT SILICON.

The element silicon exists in many forms in the earth's crust of which it constitutes about 28 per cent by weight. It is never found free, but always combined with oxygen to form silica (SiO_2), or with oxygen and metallic oxides to form silicates, of which feldspar ($\text{K}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), and kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) are typical.

The element silicon is of interest only theoretically. It can be prepared from several of its compounds without much difficulty, and, when free, exists in several allotropic forms, as does carbon in charcoal and diamond. It combines very energetically with many substances. At ordinary temperatures fluorine unites with it to form silicon tetrafluoride. It is attacked by chlorine, bromine, and nitrogen at 430° , 500° , and 1000° , respectively. When heated to 400° in the air, it burns, forming a white powder, SiO_2 or silica, the principal constituent of sand-lime bricks.

SILICA (SiO_2).

This compound occurs as sand in all soils. It is removed from them by running water and is deposited in the beds of streams and on the bottoms of the oceans, and is later compacted into great masses of sedimentary rock, called sandstone. Silica is found also in granite and other igneous rocks, as quartz, having crystallized from the molten

magma which, upon cooling, made the rocks; and is present in many veins, where it was crystallized from solutions. Flint is a variety found in chalk deposits.

Crystalline silica exists in two forms, viz, quartz and tridymite. These two minerals resemble one another very closely. Both crystallize in the hexagonal system, are optically positive, and have a hardness of about 7 (according to Moh's scale). Both are colorless to white, brittle, and have a conchoidal fracture. In specific gravity, however, there is a marked difference; that of quartz being 2.66, while that of tridymite is 2.28 to 2.33. Moreover, tridymite is soluble in boiling sodium carbonate, while quartz (unless very finely divided) is not.

Of these two crystalline varieties of silica, quartz is stable at ordinary temperatures, while tridymite is the stable form at temperatures above 800° C. Consequently, tridymite crystallizes from fusions at high temperatures and quartz at temperatures below 800°. When quartz is heated to temperatures above 800° it becomes unstable and begins to change into tridymite. The change proceeds slowly, however, so that it is possible to study the properties of quartz much above the temperature at which it ceases to be the stable modification. The reverse transformation is also quite sluggish, so that by sudden cooling it is possible to have tridymite at ordinary temperatures even though it is not the stable form.

The purest forms of silica are colorless and fuse at a temperature of about 1700° C. When fused and allowed to cool quickly it does not crystallize, but is known as quartz glass. Quartz glass has the very remarkable property of being able to withstand sudden changes of temperature without being fractured. Vessels made of this material may be heated to redness and quenched in water without fracture. Le Chatelier¹ studied the expansion of various forms of silica at temperatures ranging from atmospheric to 1050° C. The results of his investigations are shown graphically in figure 1.

The molecular changes expressed by the expansion shown in these curves are of great significance in many industrial processes. In the manufacture of silica, or Dinas bricks great difficulty is experienced in properly hardening, owing to these changes. It is also due to their great expansibility that silica bricks are unfit for use in places where they must be heated and cooled frequently. Bricks made from clays high in sand are found to expand to such an extent in the kiln that much care must be used in heating up and cooling down the ware made from them. In a fire test on sand-lime bricks, as will be shown later, it was found that in the neighborhood of 500° there was a weakening of the bricks, due, no doubt, to this sudden expansion of the quartz. In the preparation of potters, flint, quartz rock is calcined and quenched before grinding. The volume changes produced by the sudden chilling causes the rock to be filled with a very close network of minute cracks, and consequently to grind much easier than a raw quartz.

¹ Compt. Rend. de L'Academy des Sciences, 108, 1899, p. 1046, and 109, 1899, p. 264.

Fused quartz, opal and precipitated silica are forms of amorphous silica, which is characterized by the fact that its properties are independent of the directions along which forces act. In quartz and tridymite, for example, the coefficients of expansion and of conductivity, the indices of refraction, etc., are different in different directions, whereas in amorphous silica they are the same in all directions. Further, when

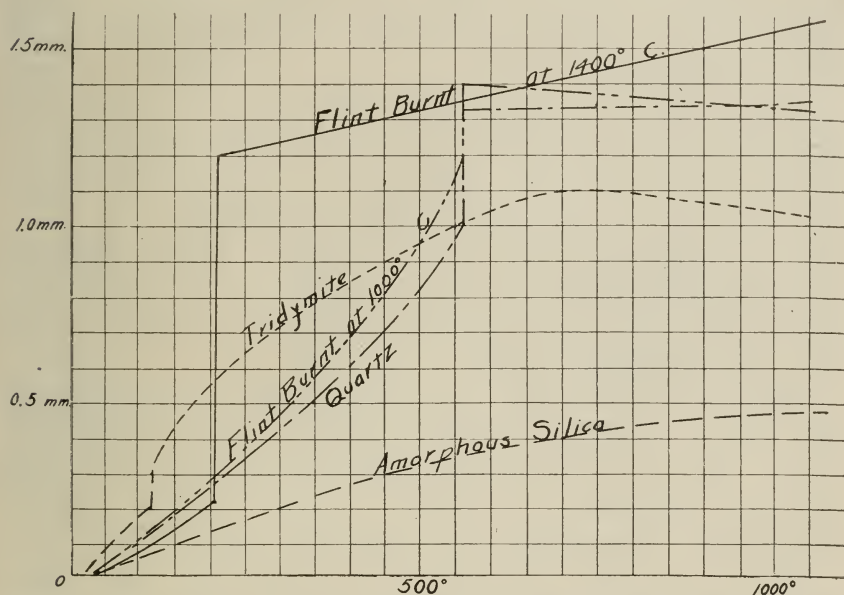


FIG. 1. Le Chatelier's curves, showing expansion of different forms of silica from 25°C. to 1050°C.

thin plates cut from opal and quartz are placed under the polarizing microscope between crossed nicols, and rotated, no color changes are observed in the opal, whereas, the quartz may show various colors, changing with the rotation of the plate.

SILICIC ACIDS AND THE SILICATES.

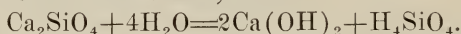
All varieties of silica, when heated with metallic compounds, combine with the metals at some temperature to form silicates. Thus a mixture of silica and sodium carbonate, hydrate or oxide, when sufficiently heated, fuses to a liquid mass, which, when cooled, dissolves in water as soluble sodium silicates. On the addition of acids, these silicates are decomposed with the liberation of more or less silicic acid, and the formation of a sodium salt of the acid used. Silicic acid is very weak when considered from the standpoint of its ability to furnish hydrogen ions, or its ability to liberate other acids from their salts, or to resist

such liberation by other acids in solution. When lime is added to silicic acid in solution, a precipitate is formed, which is calcium hydrosilicate. This is the principal ingredient in set Puzzolan cements. When carbonic acid gas is passed through water containing this compound in suspension, the calcium silicate is decomposed with the formation of calcium carbonate and the liberation of silicic acid. This phenomenon is also observed when many other weak acids are allowed to act on hydrated calcium silicates, thus showing the feebleness of some of the hydrated silicic acids.

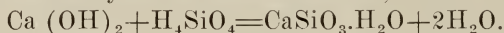
At high temperatures, on the other hand, silicic acid is one of the strongest acids known, and is able to replace many acids from their salts. This is shown in fusions of silica and sodium carbonate by the escape of carbonic acid gas. Again, in the formation of salt glazes, salt is thrown into the kiln. This volatilizes, and, coming into contact with the hot ware, is decomposed, the base being retained by the silica, while the chlorine passes out with the flue gases. Ordinary glass is a mixture of silicates formed by fusion. It resists the action of all acids except hydrofluoric. Thus, under some conditions, silicic acid forms salts that are among the weakest known, while under others it forms compounds that are very durable.

One other class of silicates that deserve mention at this point are those that set or harden when wet with water. A good representation of this class is the dicalcium silicate (Ca_2SiO_4) found in Portland cement. This compound may be formed by fusing lime and silica in the proportions indicated in the formula. It exists in several allotropic modifications,¹ distinguished as the Alpha, Beta, and Gamma varieties.

The Gamma variety is the stable form at temperatures above 1400° , the Beta between 1400° and 700° , and the Alpha below 700° . When treated with water all varieties are hydrolized with the formation of calcium hydroxide and silicic acid, thus:



The calcium hydroxide and silicic acid may react under favorable conditions to form a hydrated calcium silicate, thus:



The compounds of silicic acid found in nature are varied and numerous. When a silicate such as the dicalcium silicate mentioned above, or sodium silicate, formed by the fusion of silica and sodium carbonate, is treated with an acid, orthosilicic acid (H_4SiO_4) is formed. By carefully drying, this can be deprived of half its water, when metasilicic acid results.



By the elimination of water from 2, 3, and 4 molecules of the ortho-acid, it is possible to imagine the formation of a large series of acids. The following is a list of hypothetical acids whose salts are widely distributed in the silicate minerals.

¹Jour. Am. Chem. Soc. Vol., 28, 1906, p. 1039.

TABLE 2—*List of hypothetical silicic acids, with their formulas.*

Formula.	Name.	Basicity.
H_4SiO_4	Orthosilicic acid.....	4
H_2SiO_3	Metasilicic acid.....	2
$H_2Si_2O_4$	Metadisilicic acid.....	2
$H_6Si_2O_7$	Orthodisilicic acid.....	6
$H_2Si_3O_7$	Dibasic trisilicic acid.....	2
$H_4Si_3O_8$	Trisilicic acid.....	4
$H_8Si_3O_{10}$	Trisilicic acid.....	8
$H_2Si_4O_9$	Tetrasilicic acid.....	2
$H_6Si_4O_{11}$	Tetrasilicic acid.....	6
$H_{10}Si_4O_{13}$	Tetrasilicic acid.....	10

The following table is a list of typical minerals and their corresponding silicic acids:

Minerals and their silicic acids.

Orthosilicates (H_4SiO_4)	Garnet, Mica, Kaolin,	$Ca_3Fe_2(SiO_4)_3$ $KH_2Al_3(SiO_4)_3$ $H_2Al_2(SiO_4)_2H_2O$
Metasilicates (H_2SiO_3)	Wollastonite, Beryl, Enstatite,	$CaSiO_3$ $Gl_3Al_2(SiO_3)_6$ $MgSiO_3$
Orthodisilicate ($H_6Si_2O_7$)	Serpentine,	$Mg_3Si_2O_7$
Trisilicate ($H_4Si_3O_8$)	Orthoclase,	$KAlSi_3O_8$

LIME AND OTHER CALCIUM COMPOUNDS.

This very important constituent of sand-lime bricks is an oxide of the metal calcium, some of the compounds of which are found in large quantities in nature. It exists principally in combination with carbonic acid as calcium carbonate. The purest form of calcium carbonate is known as calcite, which in some localities is found in a state of almost absolute purity. Aragonite is another form of crystallized calcium carbonate, less widely distributed than calcite. The sources of the calcium carbonate for use in lime burning are the rocks, marble and limestone. These vary widely in the degree of purity in which they are found. Impure, clay-containing limestone and marls are used extensively in the manufacture of hydraulic limes and cements.

Metallic oxides vary widely in their ability to hold carbon dioxide. The carbonates of silver, mercury, iron, and lead decompose quite readily giving off carbon dioxide with the formation of the oxides, while the carbonates of the alkali metals (sodium and potassium) volatilize without decomposition. When, however, calcium carbonate is enclosed in a tube and heated in a vacuum, it is found to give definite pressures, varying with the temperature. The dissociation of calcium carbonate was first studied by Debray,¹ who observed the pressures corresponding to the boiling or melting points of various substances. The results of his work for calcium carbonate were as follows:

¹ Compt. Rend. Vol. 64, 1867, p. 603.

TABLE 3—*Vapor pressures of CaCO_3 at various temperatures, according to Debray.*

Temperature in degrees centigrade.	Pressure in mm. of mercury.
350.....	Imperceptible.....
440.....	Nearly imperceptible.....
860.....	85.....
1040.....	520.....

Le Chatelier took up the problem twenty years later (1887), after the invention of his thermo-electric couple. By means of this he was able to measure temperatures more accurately than was Debray, and furthermore, to make his curve continuous over the range of temperatures studied. His work has proved a classic, and is today among the best in this field. His results are shown in the following table:

TABLE 4—*Dissociation pressures of calcium carbonate, according to Le Chatelier.*

Temperature, in degrees centigrade.	Pressure in mm. of mercury.
547.....	27.....
610.....	46.....
625.....	56.....
740.....	255.....
745.....	289.....
810.....	678.....
812.....	753.....
865.....	1333.....

In 1897 A. Herzfeld¹ worked along a somewhat different line. He heated calcium carbonate in an atmosphere of carbon dioxide, and noted the temperature at which the carbonate began to lose weight. He came to the conclusion that at 900° the dissociation pressure of calcium carbonate is less than one atmosphere.

Otto Brille² (1905) employed the same method as did Herzfeld, but arrived at different conclusions. According to this investigator, the temperature at which the dissociation pressure of calcium carbonate is equal to an atmosphere is 825°.

The latest work on the subject is that of D. Zavrieff,³ who carried out a series of very carefully conducted measurements, and arrived at the conclusion that 910° to 920° is the temperature at which the dissociation pressure of calcium carbonate is equal to an atmosphere; and of E. H. Reisenfeld,⁴ who finds that at 700°, 800° and 900° the dissociation pressures are respectively 50.4 mm., 195 mm. and 700 mm. In the light of this recent work, it appears to be advisable to adopt 900° as the temperature of rapid decomposition of calcium carbonate.

¹ Zeitschr. für Rübenz Ind., 1897, p. 820.

² Zeitschr. für anorg. Chem., vol. 45, 1905, p. 275.

³ Jour. de chimie physique, vol. 7, 1909, p. 31

⁴ Jour. de chimie physique, vol. 7, 1909, p. 561.

As viewed in the light of the phase rule, we have in the equilibrium $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2 - 43741 \text{ cal.}$ a univariant system, by which we mean that a change in the temperature of the system necessitates a corresponding change in pressure and vice versa. If the temperature is kept constant, reduction of the pressure of the carbon dioxide will result in the formation of more of the gas. It will be noticed that heat is absorbed when the reaction proceeds toward the right and evolved when it goes in the opposite direction; and, further, that for every 100 grms. of CaCO_3 decomposed 43741 cal. of heat are rendered latent.

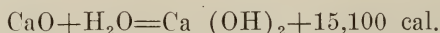
If we examine this reaction further in the light of the principle of Le Chatelier, we are enabled to predict the direction in which the equilibrium will be shifted by any external change. This law states that when any external influence is brought to bear on a system in equilibrium so as to cause a change in that equilibrium the direction of the change will always be such as to minimize the effect of the external influence. Consequently, if we raise the temperature, the reaction will proceed in a direction so as to absorb heat. If we attempt to increase the pressure of carbon dioxide, this gas will be absorbed, etc.

The decomposition of calcium carbonate is greatly accelerated by the passage of a current of air or steam through the kiln so that a much lower temperature can be used in burning than would otherwise be the case. It will be noticed from the table that at 812°C. the pressure of carbon dioxide is 753 mm. or nearly one atmosphere. Now, if limestone be heated to this temperature in a kiln with no draught there will be very little decomposition. The carbonate will decompose, giving off carbon dioxide until the atmosphere of the kiln becomes saturated with this gas or until the partial pressure of the gas is equal to the dissociation pressure of the calcium carbonate, when the reaction will cease until some of the carbon dioxide is removed and the partial pressure of the gas is thus reduced. If, on the other hand, a current of air or steam be passed through the kiln heated to this temperature, the carbon dioxide will be carried away as fast as it is formed, and the partial pressure of this gas will not be permitted to rise to a point where it prevents the dissociation of the calcium carbonate. At a temperature somewhat higher than 900°C. the pressure of carbon dioxide is greater than atmospheric pressure, consequently dissociation will go on rapidly so long as the gas is permitted to escape, regardless of whether or not there is a draught through the kiln.

The dissociation of calcium carbonate may be compared to the evaporation of water. As the vapor pressure of water increases with the rise in temperature, so does the dissociation pressure of calcium carbonate. At 100° the vapor pressure of water is equal to the atmospheric pressure, while the pressure of CO_2 from CaCO_3 is equal to an atmosphere at about 900° . If a flask containing a few cubic centimeters of water be heated to a temperature below 100° , the water will evaporate slowly; whereas, if a current of dry air be drawn through it, the water will evaporate rapidly, just as it would in an open dish with the wind blowing over its surface. When heated to 100° water passes off rapidly

as vapor, regardless of the kind of vessel in which it is heated, or any other condition, save the rate at which heat is supplied. The rate of evaporation is dependent on the ability of the vapor to get away; under the conditions first described, it could get away only by diffusion through the air; while in the presence of the current of air, it is carried off. In the burning of lime, we have an exactly similar phenomenon. At 900° the reaction proceeds rapidly, dependent only on the rate at which heat is supplied. This temperature corresponds to the boiling point in a liquid, since decomposition proceeds rapidly only so long as heat is supplied and the gas is free to escape into the atmosphere. At lower temperatures, on the other hand, the decomposition proceeds only so long as the gases resulting from the decomposition are removed in some way, and their pressure is kept below that of the carbon dioxide resulting from the decomposition of the calcium carbonate.

Calcium oxide, when treated with water, reacts according to the equation:

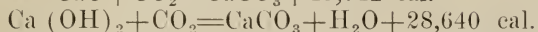


It will be seen from the equation that this reaction proceeds with the evolution of heat, and that the amount of heat evolved is one-third of that required to effect the decomposition of calcium carbonate.

The ease with which water combines with calcium oxide is influenced by the presence of impurities and by the temperature at which the lime was burned. Very pure lime, burned from calcium nitrate, hydrates slowly, while lime burned from pure limestone, hydrates readily. Hydraulic limestones containing much clay hydrate slowly, and if the quantity of clay present is as great as 30 to 50 per cent it does not hydrate at all, unless first finely pulverized. If heated to temperatures higher than that at which the dissociation pressure is equal to the atmospheric pressure, limes may be overburned. When heated to 1600°, pure calcium oxide forms a white porcelain-like mass which may be hydrated only with difficulty. Limestones containing clay and silica are much more easily overburned than pure limestones, owing to the formation of silicates, aluminates, etc. It is very difficult to burn good lime from magnesium limestones, owing to the fact that a much higher temperature is required to decompose the calcium carbonate than the magnesium carbonate, and consequently great care is required to prevent the magnesium oxide from fritting, and at the same time to expel completely the carbon dioxide from the calcium carbonate.

On hydration, calcium oxide undergoes a change in density from about 3.13 to 2.078, and, consequently, a change in volume. The increase in the apparent volume of the oxide on changing to the hydrate is about 3½ when just the right amount of water is used. The increase varies quite considerably, however, according to the method used in slaking. This expansion on hydration explains the injurious effect of lumps of unslaked lime in bricks, mortar, cement, etc.

Both caustic and hydrated lime combine quite readily with carbon dioxide in the proportions shown by the equations,



It will be noted that when carbon dioxide combines with calcium oxide or with slaked lime heat is evolved. The partial pressure of carbon dioxide in the atmosphere is only 0.23 mm., consequently, caustic lime, when slightly heated, will not take up CO_2 from the air. If, however, lime be heated in a crucible and CO_2 be conducted over it so that the pressure of CO_2 is equal to an atmosphere, combination takes place quite readily, and the lime glows until the reaction is completed.

All these facts show that lime is a powerful base, combining easily with even the weakest acids. Silica or silicic acid and lime combine not only at high temperatures, but also at temperatures comparatively low. When a mixture of lime and finely divided silica is subjected to steam pressure, combination takes place and a hard artificial sandstone is produced. This is the reaction on which the sand-lime brick industry is based.

THE RAW MATERIALS OF THE SAND-LIME BRICK INDUSTRY.

The materials used in the manufacture of sand-lime bricks are clean quartz sand, or other material rich in silica, and lime, with the preference in favor of calcium lime rather than the magnesian variety. Bricks apparently good at the time of manufacture can be made from impure sands, but such bricks will not withstand the action of the weather so well as those in which purer sands are used.

SAND.

OCCURRENCES AND ORIGIN.

Sand is one of the products resulting from the disintegration of rocks. It may, therefore, be composed of many different kinds of minerals and consequently vary widely in chemical composition. With reference to the size of its particles, sand lies between the clays, on the one hand, and the gravels, on the other. Materials passing screens all the way from 5 to 100 mesh may properly be spoken of as sands. In some sands there is gradation of sizes, while in others the grains are all of nearly the same size. Furthermore, sand may vary widely in the character of the grains, some of them being round, while others are sharp.

Most of our soils, sands, sedimentary rocks, etc., were formed originally by the disintegration of igneous rocks. Where the molten material or lava cooled rapidly it produced obsidians or glasses of uniform composition, but not corresponding to any definite chemical formula. Where, on the other hand, the mass of material cooled slowly crystallization took place, several constituents separated as minerals, and comparatively coarse-grained rocks—of which granite is a type—resulted. In granite are distinct grains of quartz, mica, hornblende, feldspar, and several other minerals. When rocks of this kind are exposed to the action of the weather, the softer, and less resistant constituents crumble away first. Quartz, which is the most resistant of all the constituents, is left behind, and collects in stream beds as sand.

Feldspar is also found in some sands, soils, and clays, but being less resistant than quartz, it is less abundant than this mineral in the residues left by weathering. Feldspar sands, limestone sands, chalks, marls,

etc., are entirely unsuited to take the place of ordinary sand in the manufacture of sand-lime bricks. In its generally accepted sense, the term "sand" signifies quartz sand, and it is quite essential that sand should be of this character when it is to be used in the manufacture of sand-lime bricks, although, for some other purposes, such as for mortar, concrete, etc., feldspathic sands or sands of any other character will do quite well.

Sands may be variously classified according to their modes of occurrence, their origin, etc., into (1) those which have been shifted about and sorted by the winds, usually spoken of as bank sands; (2) those transported by running streams, called river sands; and (3) those occurring on lake and ocean shores, known as lake and sea sands. Beds of sand which have been formed by the grinding action of glaciers and the sorting action of glacial streams are also met with occasionally. These are called glacial sands.

Sands from all these sources are used in the sand-lime brick industry, as are also, in several instances, silica-containing materials not properly called sands. In the report on the Mineral Resources¹ of the United States for 1908, there were 74 plants reported as producing sand-lime bricks. For the purpose of securing data on various phases of the manufacture of these bricks, circular letters were mailed to each of the plants. The information obtained in response to a question as to the kind of sand used is shown in the following table:

TABLE 5—*Kind of sand used in the manufacture of sand-lime bricks in the United States.*

Number of plants using—

Bank sand.	River sand.	Lake sand.	Sea sand.	Crushed stone.	Weathered stone.	Ore tailings.	Total reporting.
29	16	3	2	6	1	1	56

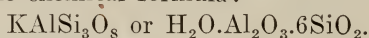
The principal materials utilized as sand in the sand-lime brick industry in this country are bank and river sands, and crushed stone. The use of tailings from copper ore is quite unusual, as is also the use of crushed granite; which was reported by one firm. However, these incidents merely show that, so far as the ability to make good brick is concerned, the origin of the material is utterly insignificant so long as it possesses the proper chemical composition.

IMPURITIES IN SAND.

The ordinary impurities found in quartz sand are silicates such as occur associated with quartz in granite and other rocks, and their decomposition products. Clay, or kaolin, is one of the most important of these

¹ Mineral Resources, U. S. for 1908, U. S. Geological Survey, 1909, p. 517.

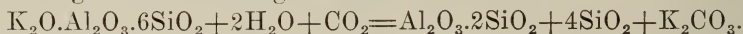
decomposition products. It results from the breaking down of feldspathic minerals, of which potassium feldspar, or orthoclase, is typical. This mineral has the chemical formula:



and the following composition:

Silica (SiO_2)64.68 per cent
Alumina (Al_2O_3)18.43 per cent
Potash (K_2O)16.89 per cent

When exposed to the action of the weather, orthoclase decomposes according to the following reaction:



The silica and potassium carbonate resulting from this action may be carried away in solution, leaving the substance $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, which is present in all clays, and which, when pure, is called kaolin, kaolinite, or clay substance. Clay substance is an almost ever present impurity in sands, as is also ferric oxide, one of the decomposition products of iron bearing minerals which are nearly always present in igneous rocks.

LIME.

IMPURITIES.

The lime intended for use in the manufacture of sand-lime bricks should be of a high grade. It should, therefore, be burned from good materials in the best manner for producing good lime.

The raw materials from which limes are burned are limestone of various degrees of purity, and marble. The impurities found in limestone and, consequently, in the burned lime, are ferric oxide, alumina, silica, and occasionally traces of other substances. When present in the limestone, these materials usually combine with the lime during burning, and so render a part of it inactive. This is especially true when heating is carried much beyond the temperature where decomposition is complete.

Magnesia is usually present in commercial limes to some extent. This oxide is quite similar to the oxide of calcium and when the lime is intended for use in mortars, plaster, etc., is not considered particularly objectionable. It is much less basic, however, than calcium oxide, and consequently it reacts with silica much less readily than pure lime, when used in the manufacture of sand-lime bricks.

Limes have been variously classified as white and gray; hot and cool; fat and lean; quick and slow. These terms are intended to distinguish between limes relatively pure on the one hand, and those containing considerable clay or magnesia on the other. They are all used in a very general way, however, so that when a lime of a particular grade is desired for a special purpose, it is necessary to specify more definitely the limits beyond which impurities may not go.

BURNING OF LIME.

In burning lime it is necessary in some way to heat the stone to a temperature of 900° or 1000° and maintain this temperature for a sufficient length of time to allow the chemical reaction, which is started by the heat, to run to completion. The processes used in burning lime are numerous. Lime was formerly burned by heaping up piles of logs and limestone and setting fire to the pile. Today, numerous types of kilns are used, which are constructed so as to make use of coal, wood, gas, etc., as fuel.

The kiln in most general use is the shaft kiln which is nothing more than a cylindrical shaft, into the top of which the fuel and stone are dumped, to pass downward as the fuel is consumed. The ashes and burned lime are removed from the bottom. Air enters at the bottom, and, becoming heated, passes upward through the kiln, thus furnishing the draught. In some cases a jet of steam, and in others a forced draught is used to aid the decomposition of the limestone. Gas is used as fuel in some plants in this country, partly because of its cheapness, and partly because of the greater ease with which the heat produced by its combustion can be so distributed through the kiln as to prevent over-burning. Plate II is a cross section of a semi-gas fired kiln designed by Theodore Gerhard. Its description may be found in the *Tonindustrie Zeitung*, No. 11, page 103, and No. 14, page 144. The advantage of this kiln over the ordinary gas-fired kiln is that the sensible heat of the gas is not lost.

COST OF BURNING LIME.

From the reaction given in a previous section of this article, it will be seen that 43741 cal. of heat are actually used (absorbed or rendered latent) by every 100 grams of calcium carbonate decomposed, or for every 56 grams of calcium oxide formed. With this as a basis, the amount of heat necessary for the formation of one ton of lime from limestone can be calculated. The heat of formation of one gram of

$$\text{CaO from CaCO}_3 \text{ is from the above equation } \frac{43741}{56} = 781.1 \text{ cal.}$$

$$\frac{9}{5}$$

This is equivalent to $781.1 \times \frac{9}{5} = 1405 \text{ B.t.u. per lb.}$

The B.t.u. value of a pound of average Illinois coal is 11,000, so that, to find the weight of coal actually required to produce the heat necessary to make a ton of lime, we have only to divide the number of B.t.u. needed by the available heat content of the fuel, or, in this case, 1405×2000

$\frac{11000}{\quad}$, which gives 0.1277 ton, or 255.6 pounds. This item in the fuel composition is fixed, and cannot be reduced by any process whatsoever. Assuming a price of \$3.00 per ton for coal, the cost of the heat actually used would be 38 cents.

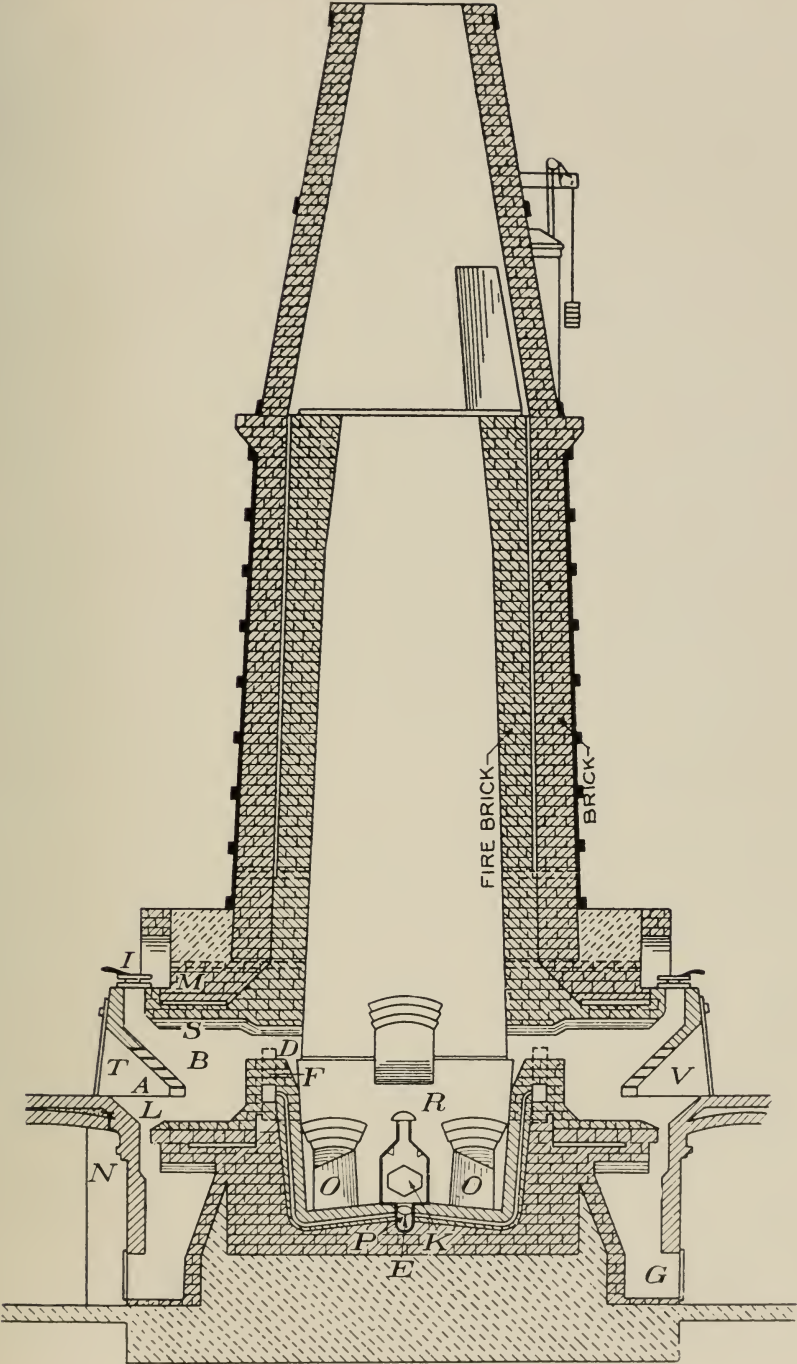
In addition to the heat used to decompose the carbonate, there are certain unavoidable losses in heat due to the fact that all products leave the kiln at a temperature higher than that at which they entered. The lime rock enters at an average temperature of perhaps 20°C. and the lime leaves it at various temperatures, depending upon the construction of the kiln. The same may be said of the fuel, of the carbon dioxide resulting from its combustion and from the decomposing carbonate, and of the nitrogen and oxygen of the air used in burning. If steam is used to help create a draft through the kiln, this too must be taken into account in the heat balance. Knowing the temperatures at which the various materials enter the kiln, the temperatures at which the products leave it and the heat capacities of the various substances, it is easy to calculate the total amount of heat employed in producing one ton of lime, and the cost of the fuel required to produce this heat. It may be said that any device which has the effect of lowering the temperature of the outgoing products will effect a saving in the cost of fuel.

MARKET GRADES OF LIME.

Caustic lime is usually shipped in the lump just as it comes from the kiln, although for some industries, as, for example, plate glass manufacturing, it is ground. When shipped as "lump" it may be either in bulk or barreled. When shipped in bulk it is wheeled from the kiln into tight box cars while still warm; the cars are closed, and sent directly to the consumer, who usually has provided his plant with an air-tight bin large enough to hold a supply of lime sufficient to last for some time. It is in this condition that lime is usually shipped for the sand-lime brick industry. When barreled, the cost is increased about 10 cents per hundred pounds. The barrels are filled and headed while the lime is still warm enough to prevent the combination with it of carbon dioxide from the atmosphere. When lime is to be ground, it is cooled and passed through a crusher which reduces it to about 80 mesh. It is claimed that crushed lime keeps better than lump lime, and that it is, moreover, easily hydrated when ready to be used. In this condition it may also be shipped in special moisture proof bags more conveniently than when in the lump condition.

Another form in which lime is now being marketed quite extensively is the hydrate, which goes under the trade name of "hydrated" or "prepared" lime. This is a very convenient form in which to handle the material; but because it weighs about one-third more than the same amount of caustic lime, it is more expensive to transport.

There are several processes in use for preparing hydrated lime. In one, a closed cylindrical shell of boiler plate steel is mounted so that it may be rotated. A charge of caustic lime with the proper amount of water to hydrate it are dumped into the cylinder through a manhole. When closed, the cylinder is rotated and hydration begins. A gage enables the operator to watch the progress of the reaction within. When hydration is complete, a valve is opened and the excess water passes off as steam, leaving a dry and completely hydrated lime.



Cross-section of semi-gas fired kiln, designed by Theo. Gerhard.

In another process a steel shell, open at both ends, is mounted like a rotary cement kiln. The quick lime and water are fed in at the upper end. As they pass downward together, hydration takes place, while a jet of superheated steam, blown in at the lower end, drives out any excess water that may have found its way down with the lime.

Numerous other processes for the hydration of lime have been patented, and some of them are in use. In these the water is added in small amounts and the hydrated lime as fast as it forms is removed by means of screens. It is evident that the dry slaking method must be used in order to prepare a dry hydrate cheaply; but by any of these processes, except the first one mentioned, where the hydration is done by steam under pressure, it does not seem improbable that some particles of caustic lime will pass through the screens and be present in the finished product. Such a lime, if used in the manufacture of sand-lime bricks, might give serious trouble unless the mixture is well siloed before pressing.

METHODS OF TESTING LIME.

In order to determine the quality of any lot of lime, resource must be had to chemical analysis, by which the exact amounts of calcium oxide, magnesium oxide, clay, unburned stone, etc., present in the sample, may be detected. Chemical analysis alone, on the other hand, will not distinguish between a properly burned lime and one which is overburned, nor between quick hydrating limes and slow hydrating varieties. Since it is very essential that the lime used in the sand-lime brick industry should hydrate readily and also that it be of the high calcium type, it is important to be able to determine these qualities rapidly and accurately.

The heat of hydration of one gram of pure calcium lime (CaO) is 269.6 calories. The heat of hydration of one gram of magnesium lime (MgO) is, on the other hand, only 135 calories, or about one-half that of pure calcium oxide. Again, it has been shown that when lime has been heated to a high temperature (1100° - 1300°) it slakes very slowly, especially when considerable clay is present. From these considerations it follows that a simple determination of the amount of heat given off on hydrating, and the time required, after the addition of water, to reach a maximum temperature, is sufficient to distinguish between a properly burned high calcium lime and all others. For this determination only very simple apparatus is required. It is necessary to have some containing vessel of suitable size, preferably with polished sides and covered with felt, wool, or some good non-conductor of heat, and a thermometer. Furthermore, some means of weighing out samples must be at hand. The determination is made by filling the vessel to be used as a calorimeter with some convenient quantity of water at a known temperature. A weighed quantity of lime is then added and the mixture is stirred, the temperature being noted at minute intervals. If the quantity of water used is 100 times the weight of the lime, the maximum rise in temperature should be about 2.5° Centigrade or 4.5° Fahrenheit

for material consisting of pure CaO . Limes well suited to the sand-lime brick industry will reach the maximum temperature quickly. When comparing various limes it is well to plot thermometer readings against

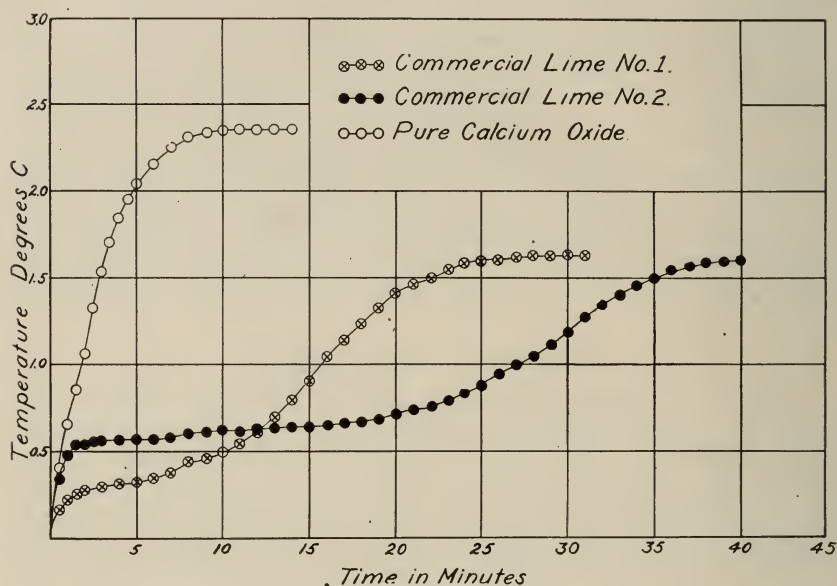


FIG. 2. Curves showing rise of temperature in the hydration of samples of lime.

time. The following curves, which are the records of tests on a pure calcium oxide and two commercial limes (Fig. 2), show how this may be done.

TECHNIQUE OF THE MANUFACTURE OF SAND-LIME BRICKS.

PROCESSES FOR PREPARING MIXTURES.

The first step in the manufacture of sand-lime bricks is the mixing of the sand and lime, and it is in this that the various processes differ. The subsequent steps—the pressing or molding and hardening of the mixture—are practically the same in all plants, except as to kind of machinery used.

According to the *Keramisches Jahrbuch*, 1909, there were in use in Germany in 1908 five processes for preparing the mixture used in the sand-lime brick industry. These were known as:

The pure hydrate methods, in which (1) burned lime is slaked (in any way) without the addition of sand, pulverized, and finally mixed with sand and pressed;

Mixed methods, in which (2) burned lime is slaked with a part of the sand, then mixed with the remainder and pressed; or (3) burned lime is partly pulverized and mixed with a part of the sand, and then placed in the silo for a while, after which it is mixed with the remainder of the sand and pressed; and,

Caustic lime methods, in which (4) the entire quantity of sand is mixed with the pulverized caustic lime in a mixing machine, and then is cured in a silo and pressed; or (5) pulverized caustic lime is mixed with all the sand in a slaking machine until a good mixture is obtained, when it is pressed.

Complete information as to the extent to which these various methods are used in Germany was not given. The results of a circular letter sent out by the Verein der Kalksandsteinfabriken relative to the matter are given in the following table:

TABLE 6—*Number of plants using various processes of preparing mixtures for sand-lime bricks.*

Method.	Number of plants.
No. (1).....	62.....
No. (2).....	21.....
No. (3).....	1.....
No. (4).....	37.....
No. (5).....	13.....

In order to get an idea of the prevailing processes in the United States, the following statement was mailed to the 131 companies, reported as being manufacturers of sand-lime bricks, with the request that each check the number which covers his process:

1. Lime is slaked before being mixed with any part of the sand.
2. Caustic lime is mixed with a part of the sand and slaked. It is then mixed with the remainder of the sand and pressed.
3. Caustic lime is finely pulverized and mixed with a part of the sand and sufficient water to completely hydrate it. It is then stored for a time in a silo, after which it is mixed with the remainder of the sand and pressed.
4. Caustic lime is finely pulverized and mixed with all the sand and sufficient water to insure complete hydration. It is then stored in a silo for a time and pressed.
5. Caustic lime is finely pulverized and mixed with all the sand. The mixture is then passed through a machine in which the lime is completely hydrated, after which it is pressed.
6. The caustic lime and a part of the dried sand are ground together. This mixture is then mixed with the remainder of the sand and sufficient water added to insure complete hydration of the lime. The mixture is then siloed for a day and pressed.

The results of this inquiry are shown in the table following:

TABLE 7—*Processes employed in preparing mixtures for the manufacture of sand-lime bricks in the United States.*

	Process No. 3.						Total reporting.
	1.	2.	3.	4.	5.	6.	
Number of plants using	29	0	3	12	2	15	61

In this country, as in Germany, more plants use the slaked-lime method than any other single one. However, if we combine 4, 5, and 6 (the caustic lime processes), the balance is in favor of this practice. The prevalence of these two processes in this country makes it seem desirable to discuss them somewhat more at length. Accordingly, under the first heading (hydrated lime methods) will be considered all those processes in which the lime is hydrated before being mixed with the sand, and under the second heading (caustic lime methods) those in which the sand is mixed with the lime in the caustic condition.

THE HYDRATED LIME METHODS.

Where process No. 1 is used the question as to the best method of slaking the lime arises. There have been many patents issued for spe-

cial methods of procedure in carrying out this operation, but they all fall into one of two classes, namely: (1) the wet, and (2) the dry slaking process.

In the wet slaking process water enough is added to the lime to form a thick paste or putty. Machines of various kinds are in use for stirring the lime so as to continually expose fresh surfaces. With properly burned fat limes the slaking takes place easily, and, if the proper amount of the water has been added, the lime swells up to a volume of about $3\frac{1}{2}$ times that of the original caustic lime. In this condition it is mixed with the sand and pressed.

It is claimed by the advocates of this method that all of the lime is completely hydrated and that each molecule of calcium oxide takes up, either chemically or otherwise, several times as much water as that required by the chemical formula of the hydrate. This phenomenon appears to take place only when the quantity of water added is just sufficient to form a thick paste. If less be added the temperature rises high enough to expel the water, which might otherwise be retained, while if too much be added the temperature is kept down to a point where the oxide appears to be unable to take up more water than that required by the chemical formula. This increase in volume and plasticity enables the lime to envelope the sand grains more completely than is the case when dry slaking method is used. On the other hand, the mixing is more expensive in that more power is required and the process cannot be completed so quickly. Again, there is no chance to screen lime slaked by the wet method, consequently lumps of unburned or overburned lime are apt to get into the bricks, thus injuring their quality.

In the dry slaking process just enough water is added to give a dry product. By this method it is possible to screen out lumps of unslaked or improperly burned lime. Mixing is also easily accomplished, but it is doubtful whether the sand particles are as completely surrounded by the lime in this method as in the wet slaking process. In this method, however, there is a possibility of fine particles of caustic lime passing through the screen so that unless the mixture is well siloed before pressing, trouble is liable to occur due to subsequent hydration in the hardening cylinder.

THE CAUSTIC LIME METHODS.

There are several methods of procedure employed in the caustic lime processes. According to one method pulverized caustic lime is mixed with the sand, or a part of it, and enough water is then added to slake the lime and give the mixture the proper consistency for the press. The mixture may pass directly to the press as in process No. 5, or be stored in a silo to cure.

Process No. 6 is that of the American Sand-Lime Brick Machinery Company. It is a caustic lime process in which a part of the dried sand is ground with the caustic lime to a fine flour, which is then mixed with the remainder of the sand, wet to the proper consistency, and sent

to the silo until cured. It is evident that by grinding the lime with a part of the sand perfect mixing is effected, and at the same time each particle of sand is surrounded with a film of lime. When this ground mass is later mixed with the remainder of the sand, the tendency to ball up and form lumps is avoided. Again, it is claimed that by grinding the lime and sand together the manufacturer is practically assured that all the lime that remains in the mixture will be reduced to a size so small that no damage will result from its being incorporated in the brick.

It will be evident from what has been said that in the caustic methods wet sands may be worked without much inconvenience, as the moisture in the sand will be taken up by the caustic lime. When this procedure is adopted, however, none but the best quick slaking limes should be used, for if magnesian limes are used, even if siloed for 24 hours, there is a possibility of improper hydration in the mixture and consequent swelling and rupture of the bricks while in the hardening cylinder.

PREPARATION OF THE SAND.

It is generally believed that an assortment of various sizes of sand is advantageous in the manufacture of sand-lime bricks. In many localities sands occur in which the proper proportion of fine and coarse material is already present, and in others access may be had to several banks some of which are fine and others coarse. Where such is not the case, however, the practice of grinding a part or all of the sand is commonly resorted to. The following table is given to show to what extent sand grinding is practiced in the United States:

TABLE 8—*Practice in regard to grinding sand for sand-lime bricks in the United States.*

	Proportion of sand ground.									Total reporting.
	None.	All.	Some.	$\frac{1}{2}$.	$\frac{3}{4}$.	$\frac{1}{4}$.	$\frac{1}{5}$.	$\frac{1}{6}$.	$\frac{1}{10}$.	
Number of plants.....	29	10	10	4	3	3	1	1	2	63

The question of fineness of sand used in the manufacture of brick is one that has received considerable attention both in this country and abroad. Some ten years ago Professor E. Gasenapp¹ of the Polytechnic Institution at Riga published a paper in which he described two series of tests, in one of which he used a high calcium lime and in the other a dolomitic lime. He employed also two grades of sand, one, a coarse sand 0.6 to 1.0 mm. in diameter, and the other a fine sand 0.2 to 0.3 mm. in diameter. One sample of each lot of sand was treated with 10 per cent of lime and another sample with 20 per cent of lime, and each mixture was subjected to high and low steam pressure. The results of this work are tabulated as follows:

¹ Tonindustrie Zeitung, vol. 24, 1900, p. 1703 and vol. 25, 1901, p. 762.

TABLE 9—*Series A—Analyses of briquettes in which pure lime was used.*
(Analyzed after exposure of eight hours in steam cylinder.)

Number.	Mixture.	Steam pressure in atmospheres.	Total CaO.	Ca(OH) ₂ from total.	MgO.	Al ₂ O ₃ +Fe ₂ O ₃ .	CO ₂ .	Chemically combined water.	Soluble SiO ₂ .	Sand.	Total.
1	90 parts coarse sand; 10 parts lime.	5	6.50	1.67	3.45	0.88	0.43	89.10	100.37
2	Same as No. 1.....	10	9.38	1.24	0.42	2.54	2.96	3.33	82.00	100.63
3	80 parts coarse sand; 20 parts lime..	5	16.69	7.16	4.77	2.78	0.59	74.67	99.50
4	Same as No. 3.....	10	16.59	6.05	0.29	3.02	4.60	2.75	72.85	100.10
5	90 parts fine sand; 10 parts lime.....	5	8.74	0.85	0.31	3.75	1.79	3.06	82.02	99.67
6	Same as No. 5.....	10	10.10	0.58	0.56	2.23	2.55	7.58	76.88	99.40
7	80 parts fine sand; 20 parts lime....	5	15.81	4.23	0.31	5.21	3.90	3.41	70.68	99.32
8	Same as No. 7.....	10	17.67	0.98	0.65	3.13	3.59	11.14	63.05	99.42

TABLE 10—*Series B—Analyses of briquettes in which dolomite lime was used.*
(Analyzed after exposure of eight hours in steam cylinder.)

Number.	Mixture.	Steam pressure in atmospheres.	Total CaO.	Ca(OH) ₂ from total.	MgO.	Al ₂ O ₃ +Fe ₂ O ₃ .	CO ₂ .	Chemically combined water.	Soluble SiO ₂ .	Sand.	Total.
1	90 parts coarse sand; 10 parts dolomite.....	5	4.98	0.38	3.81	0.23	2.21	2.24	0.75	85.23	99.45
2	Same as No. 1.....	10	4.49	0.43	3.45	0.96	2.05	2.13	3.14	83.61	99.83
3	80 parts coarse sand; 20 parts dolomite.....	5	8.56	2.53	6.58	0.70	3.38	3.44	0.65	75.80	99.11
4	Same as No. 3.....	10	9.97	1.92	7.57	0.95	3.19	4.39	1.69	72.62	100.18
5	90 parts fine sand; 10 parts dolomite.....	5	4.97	0.92	3.75	0.68	2.22	1.82	1.98	84.23	99.65
6	Same as No. 5.....	10	5.40	0.40	4.07	0.95	1.92	1.88	6.29	79.28	99.79
7	80 parts fine sand; 10 parts dolomite.....	10	9.23	0.79	7.00	0.94	1.82	5.74	7.03	67.88	99.64

TABLE 11—*Summary of results indicated in preceding tables of analyses.*

Percentage of caustic filler used.	Pressure of steam in atmospheres.	Kind of caustic filler used.	Percentage of soluble silica found by analysis of product.	
			Using coarse sand.	Using fine sand.
10.....	5	Pure lime.....	0.43	3.06
		Dolomite lime.....	0.75	1.98
	10	Pure lime.....	3.33	7.58
		Dolomite lime.....	3.14	6.29
20.....	5	Pure lime.....	0.59	3.41
		Dolomite lime.....	0.65
	10	Pure lime.....	2.75	11.14
		Dolomite lime.....	1.69	7.03

S. V. Peppel¹ in 1903 studied the effect of varying the amount of fine and coarse sand employed in the mixture. He used two pure sharp glass sands with mechanical analysis as follows:

Coarse sand:

Retained on sieves of following meshes:

	Per cent.
20	0.0
40	50.0
60	33.0
80	7.0
100	7.0
120	2.0
150	1.0

Fine sand:

Residue on sieves of following meshes:

	Per cent.
120	1.70
150	1.00
200	1.25

Average diameter of grains:

0.0212 in.	24.00
0.0086 in.	19.00
0.0004 in.	8.50
0.00026 in.	7.50
0.000136 in.	5.70
Finer	32.35

In each mixture 5 per cent of steam-slaked calcium hydrate was used. The results, each being the average of three tests, are shown in the following table:

¹ Proc. Am. Ceramics Soc., vol. 5, 1903, p. 168.

TABLE 12—*Effect of coarseness of sand used in sand-lime brick mixtures.*

Number.	Ratio of coarse to fine grains.	Crushing strength of resulting briquette in lbs. per square inch.	Tensile strength of resulting briquette in lbs. per square inch.
77.....	3 coarse : 2 fine.....	3114	131
79.....	4 coarse : 2 fine.....	2955	144
84.....	3 coarse : 2 fine.....	2451	224

Gasenapp's tables show clearly that fineness of grain is a factor determining in part the completeness of the reaction. Since this is so, the fineness of the sand employed in the mixture is the index of the value of the finished product. This view seems to have been accepted and adopted, in principle at least, by the majority of manufacturers. Even those who do not grind, may, in the majority of cases, have at hand a natural product sufficiently supplied with fine material to answer the requirements of this theory. Peppel's tables show, however, that the use of fine sand is accompanied by lowering in the quality of the bricks made from it, at least in some respects, as, for example, in their crushing strengths. Hence it would seem that these two series of experiments lead to contradictory results. At any rate, further experimentation is necessary in order properly to interpret the condition involved. First and foremost, it seems a study should be made of the compounds formed by the reaction, that is, of the bonding material of the bricks. Has it properties of such value that a greater amount will add to the ultimate value of the mass, or has it objectionable features which would indicate that it should be kept down to the minimum point in the ultimate product? Other considerations also naturally suggest themselves as subject for study—for example, the shape of the sand particles used.

From an examination of the experiments originally conducted on the finely-divided silica of Southern Illinois, referred to on page 9, it appeared evident that a further study along the same line might show that the homogeneous hydrosilicate, thus easily produced at will and in any desired form, would afford convenient material for the study of its properties.

An investigation was therefore undertaken for the purpose of learning more about the properties of silicates made from very fine silica, the effect upon them of the introduction of varying amounts of the silica into the mixtures used in their manufacture, and of the relative values of round and sharp sand. The writers prepared bricks from the mixtures shown in the following tables. The silica used was the finely-divided material from Southern Illinois, which is in reality a very finely divided quartz. When properly mounted and examined under the polarizing microscope at a magnification of about 300 diameters, the silica exhibits very distinctly the crystalline structure of quartz. A few particles, measured by means of a micrometer eye-piece, show diameters in excess of 0.02 mm. or .0008 in. The bulk of the material, however, is composed of particles less than 0.01 mm. or .0004 in. in diameter. For comparison of their sizes with the finer particles used by Peppel, see page 36.

TABLE 13—*Composition of mixtures used by Parr and Ernest in the manufacture of test bricks.*

(First series)

No.	Kind of sand used.	Sand.		Lime.		Silica.	
		Weight.	Per cent.	Weight.	Per cent.	Weight.	Per cent.
1	Round.....	23.75	95	1.25	5	-----	-----
2	Sharp.....	23.75	95	1.25	5	-----	-----
3	Round.....	22.50	90	1.25	5	1.25	5
4	Sharp.....	22.50	90	1.25	5	1.25	5
5	Round.....	22.75	91	1.75	7	0.50	2
6	Sharp.....	22.75	91	1.75	7	0.50	2
7	Round.....	22.25	89	2.00	8	0.75	3
8	Sharp.....	22.25	89	2.00	8	0.75	3
9	None.....	-----	-----	5.00	20	20.00	80
10	None.....	-----	-----	7.50	30	17.50	70
11	None.....	-----	-----	10.00	40	15.00	60
12	None.....	-----	-----	12.50	50	12.50	50

TABLE 14—*Composition of mixtures used by Parr and Ernest in the manufacture of test bricks at Anderson, Indiana. Figures show percentages.*

(Second series)

Number.	Round sand.	Sharp sand.	Fine sand—60-100.	Fine silica.	Kaolin (clay).	Lime (CaO).	Number of bricks made.
1.....	92	-----	-----	-----	-----	8	8
2.....	-----	92	-----	-----	-----	8	9
3.....	90	-----	2	-----	-----	8	8
4.....	-----	90	2	-----	-----	8	8
5.....	90	-----	-----	-----	2	8	8
6.....	-----	90	-----	-----	2	8	8
7.....	87	-----	5	-----	-----	8	8
8.....	-----	87	5	-----	-----	8	8
9.....	87	-----	-----	-----	5	8	7
10.....	-----	87	-----	-----	5	8	8
11.....	85	-----	5	2	-----	8	8
12.....	-----	85	5	2	-----	8	8
13.....	84	-----	7	1	-----	8	8
14.....	-----	84	7	1	-----	8	8
15.....	80	-----	8	2	-----	10	7
16.....	-----	80	8	2	-----	10	8
17.....	-----	-----	90	-----	-----	10	10
18.....	25	-----	66	-----	-----	9	8
19.....	-----	-----	92	-----	-----	8	9
20.....	-----	-----	85	-----	-----	15	10
21.....	25	25	40	-----	-----	10	8

In pressing, a small-sized brick press, belonging to the Anderson Foundry & Machine Company, Anderson, Indiana, was used, and steaming was done in a small experimental hardening cylinder belonging to the same firm. The bricks were kept under 8 atmospheres of steam pressure for 10 hours.

All the bricks made were tested, with the results shown below:

TABLE 15—*Results of tests on experimental bricks.*
(First series)

No.	Composition.				Results of tests.				
	Sand.		Lime, per cent.	Silica, per cent.	Crushing strength in lbs. per square inch.	Trans- verse modulus of rup- ture.	Number of bricks tested.	Absorp- tion in per cent.	Free lime, in per cent.
	Kind.	Per cent.							
1.....	Round...	95	5	-----	4,790	736	1	8.95	0.10
2.....	Sharp...	95	5	-----	3,115	467	4	12.70	0.10
3.....	Round...	90	5	5	2,420	228	4	10.81	0.14
4.....	Sharp...	90	5	5	2,626	297	4	12.31	0.22
5.....	Round...	91	7	2	1,228	71	4	13.60	1.55
6.....	Sharp...	91	7	2	2,030	367	5	16.15	0.46
7.....	Round...	89	8	3	1,240	166	4	14.30	1.36
8.....	Sharp...	89	8	3	1,688	289	5	18.91	0.59
9.....	-----	-----	20	80	1,732	137	5	41.70	0.75
10.....	-----	-----	30	70	1,470	152	4	48.00	1.97
11.....	-----	-----	40	60	1,633	416	3	32.95	3.14
12.....	-----	-----	50	50	1,440	366	3	38.70	9.43

TABLE 16—*Results of tests on experimental bricks.*
(Second series)

Tests were made on six bricks. The figures given are the means of five of these.

No.	Composition.						Tests.		
	Round sand (20-30 mesh)— Per cent.	Sharp sand (20-30 mesh)— Per cent.	Fine sand (60-100 mesh)— Per cent.	Fine silica (pow- der)— Per cent.	Kaolin (clay)— Per cent.	Lime (CaO)— Per cent.	Trans- verse modulus of rup- ture.	Crushing strength, in lbs. per square inch.	Absorp- tion, per cent of dry brick.
1.....	92	-----	-----	-----	-----	8	0	590	14.9
2.....	-----	92	-----	-----	-----	8	118	1,250	16.9
3.....	90	-----	2	-----	-----	8	0	520	12.7
4.....	-----	90	2	-----	-----	8	207	1,360	17.4
5.....	90	-----	-----	-----	2	8	0	510	13.4
6.....	-----	90	-----	-----	2	8	179	1,240	15.5
7.....	87	-----	5	-----	-----	8	155	1,390	10.5
8.....	-----	87	5	-----	-----	8	251	1,920	13.5
9.....	87	-----	-----	-----	5	8	50	790	11.7
10.....	-----	87	-----	-----	5	8	150	1,640	12.4
11.....	85	-----	5	2	-----	8	147	1,600	13.9
12.....	-----	85	5	2	-----	8	281	2,500	14.3
13.....	84	-----	7	1	-----	8	137	1,870	11.6
14.....	-----	84	7	1	-----	8	347	2,290	13.5
15.....	80	-----	8	2	-----	10	181	2,690	10.7
16.....	-----	80	8	2	-----	10	560	2,010	14.7
17.....	-----	-----	90	-----	-----	10	420	2,450	16.3
18.....	25	-----	66	-----	-----	9	598	3,640	12.8
19.....	-----	-----	92	-----	-----	8	614	3,270	15.1
20.....	-----	-----	85	-----	-----	15	174	1,180	23.2
21.....	25	25	40	-----	-----	10	391	2,650	13.7

The first desideratum in the preparation of the mixture for the manufacture of sand-lime bricks is to proportion its various ingredients in such a manner, that as little difficulty as possible will be experienced

in pressing. In order to accomplish this, several conditions must be kept in mind, viz, the strength and trueness of shape of the bricks in the green condition, and the effect of the material on the lining of the mold boxes. Sand is naturally very hard on machinery, but under some conditions it cuts much worse than under others. In our experiments we found it very difficult to press shapely bricks from a mixture of round sand and 5 per cent of lime. With 8 per cent of lime, however, the bricks were firm enough to be handled easily in the green condition. The ideal mixture, and the one that must be realized if bricks are to be made successfully on a commercial basis, is one in which there is enough fine material to surround the larger particles, thus preventing their cutting action, and to allow of very closely packing. However, it is not desirable to have all of the sand very fine. This is shown by our experience with mixtures of Illinois silica and lime. When such mixtures are put through the press in the usual way the air has not time to escape, and consequently the brick ruptures when the pressure is released from the mold boxes.

The bricks made in both series of experiments were tested in the usual way. It was not possible to measure the pressure applied in molding, but it was the intention of the operator to so regulate the depth of the mold box that each brick would be subjected to the same amount of pressure.

The results of the experiments show that brick No. 1 in the first series of tests possessed the highest modulus of transverse fracture and the greatest crushing strength. Moreover, it was lowest in absorption. No. 1 in the second series was less satisfactory. This lack of strength in the second brick may be explained by the fact that very great pressure had to be used in order to get a brick at all in the first instance, while in the second, the additional amount of lime used made the brick stronger in the green condition; but it interfered with the formation of the bond. The absorption is considerably higher in every case where the sharp sand was used, but with the exception of No. 1 of the second series, the brick made from sharp sand showed greater strength. The last four bricks of the second series are very instructive illustrations of the effect of very fine material. The absorption in these was excessively high and the bricks were weak. Two per cent of clay has apparently no effect on the strength of the bricks, while 5 per cent of this substance weakens them but lowers the absorption. Too much lime weakens the bond and increases the absorption, as shown by Nos. 17, 19, and 20.

Our study of bricks made from lime and fine silica indicates that the bonding material is the weakest part of the brick, and that, for the best results, the bond should be kept as low as possible, consistent with good bonding.

The statistics on page 34 show that more than half of the plants operating in this country grind a part of the sand and that 10 out of 63 grind it all. In view of the fact that sand grinding is a very difficult and expensive process, it must be evident that the followers of this practice expect great good to come from having the material very fine.

It is the intention of some operators to crush the material until all of it will pass the 100-mesh screen. When grinding is carried to such an extent it will be evident that a large part of the sand will be so finely divided that it will compare favorably with the fine Illinois silica which has been used as the basis for the preparation of compounds for this investigation.

One of the purposes of this work was to study the character of compounds made from extremely fine material, and in the bricks numbered 9, 10, 11, and 12, we have this condition realized. A glance at the results presented in the preceding table will show that despite the fact that excessively large amounts of lime were used in these bricks, they were of a poor grade. Those samples in which smaller quantities of lime were employed lacked coherence. (See plate III.)

It would seem that where the material is very finely divided the molecular ratio of lime to silica required for a satisfactory product should be nearly one. It can be readily seen that the finer the sand, the greater is the amount of lime required to yield a coherent mass. If the sand particles are to be welded together by the steaming process, it is evident that each must be surrounded by a film of lime. If we assume that this film is of uniform thickness, then the amount of lime needed to produce the bond will be directly proportional to the total surface of the particles and inversely proportional to the square of their mean diameters. This relation, however, holds only to a point beyond which the sand grains are so small that the reaction penetrates their masses and converts the entire mixture into a homogeneous calcium silicate. Our experiments show that when very fine silica was used in the mixture the amount of lime necessary to give a strong coherent mass was nearly equal to that of the silica used.

From the foregoing discussion it would seem that to make the best bricks with the minimum amount of lime the aim of the manufacturer should be to keep the ratio of quartz to bond in his brick as high as possible. To effect this, however, there must be a gradation in the size of the sand used from coarse to that which will just pass a 100-mesh sieve. The use of very much material finer than this is not advisable, since it would increase the amount of porous bonding material. Figures A and B of plate IV are photographs of magnified sand-lime brick sections, as seen in polarized light. The relatively large amount of bonding material in figure B, as compared with that in figure A, is noticeable.

No fixed rule can be laid down for the proper proportioning of the various sizes of sand, since this is a matter that will depend largely on the peculiarities of each particular sand. It may be stated, however, that in any case sizes ranging from about 60 to 100 mesh should predominate, with only enough of the finer particles to occupy the interstices between the larger ones.

While it is true that in some respects the bricks made from round sand were the best, it must be remembered that there are other considerations to be weighed in any final conclusion as to the best condition in which to have the sand. In our experiments there was some difficulty

in pressing the bricks in which the round sand was used, and in the case of the first sample this operation was almost impossible. The photographs in plate III show the effect of handling bricks in which round and sharp sands were used. Those in which round sand was used are worn at the corners and their sides are rough, while the others, made with sharp sand, retain their sharp corners and have smooth sides.

CONCLUSIONS.

From a consideration of our own experiments and a study of the literature on the subject, the following conclusions with reference to the character of the sand used in mixtures for sand-lime brick appear to be warranted:

1. Sand or silica may be brought to such a degree of fineness that the reaction with lime will proceed throughout the particles, forming a homogeneous hydrosilicate with distinctive properties which are imparted to the brick in direct proportion to the amount of such material present.
2. Some fine material is necessary in order to give the mixture a consistency such that it will mold easily into bricks, which in the green condition will be strong enough to be handled.
3. The properties of the compound resulting from the interaction of lime and very fine silica are not desirable in a building brick, and consequently in sand-lime brick the amount of this compound present in the brick should be kept as low as possible.
4. The quantity of lime needed to give a strong coherent mass will vary directly as, (a) the surface factor of the sand particles; and (b) the amount of superfinely divided silica.
5. The character of the sand particles (whether round or sharp) must be considered from the standpoint of the effect on both the green brick and the finished product. The best condition would appear to be found in a mixture of both round and sharp sand.

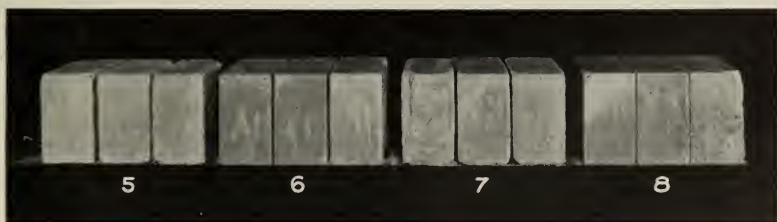
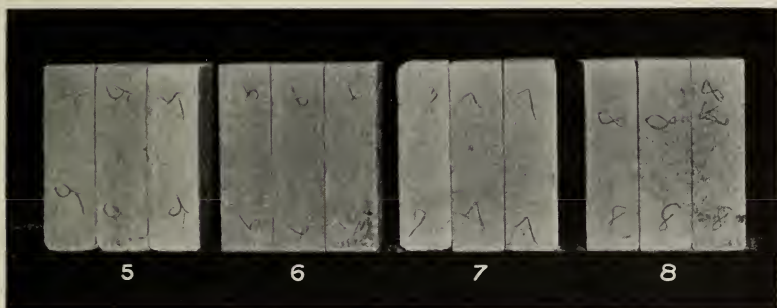
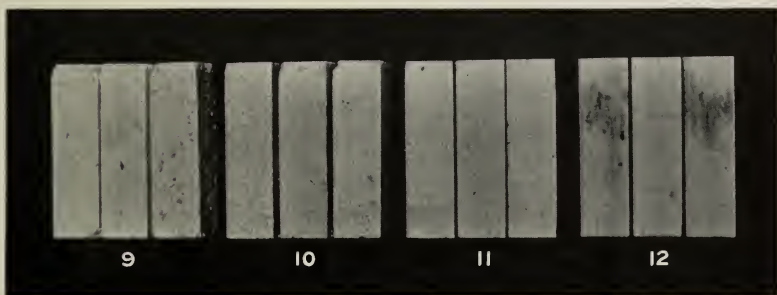
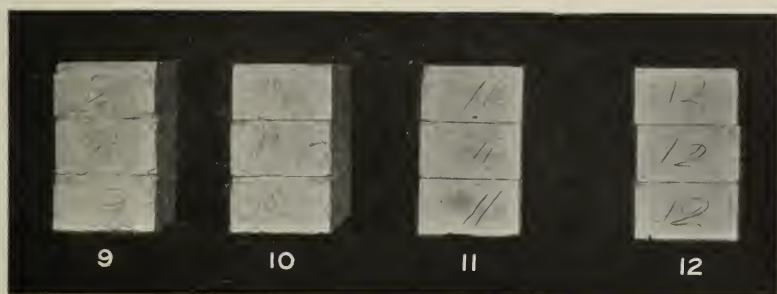
THE EFFECT OF IMPURITIES IN SAND.

The effect of clay upon the quality of sand-lime bricks has been studied by S. V. Peppel,¹ who concludes that this constituent, when not in excess of 10 or 12 per cent of the mixture, is not injurious to the bricks. On the other hand, it adds to the ease with which the bricks may be molded, and consequently, in small amounts, may be considered beneficial rather than detrimental² to the mixture.

Since kaolin is the base of all clays, Peppel in his experiments used this as representing the hydrated silicates. Feldspar was employed as representing the anhydrous silicates. The following tables are reprinted from Peppel's paper:

¹ Proc. Am. Ceramic Soc., vol. 5, 1903, p. 168.

² A glance at the table on page 38 will show that while the substitution for 2 per cent and 5 per cent of the coarse sand in the mixture of an equal quantity of kaolin proves beneficial to the bricks, the beneficial effect is not as great as if fine sand had been used in its place.



Photographs of sand-lime bricks containing fine-grained quartz, and different proportions of lime.

TABLE 17—*Effect of clay in sand-lime brick mixtures upon the quality of the resulting bricks.*

(By S. V. Peppel)

Data:

Steam pressure—150 pounds per square inch.

Temperature in hardening cylinder—185° C.

Time exposed to steam—10 hours.

Molding pressure—10,000 pounds per square inch.

Number of test.	Composition of mixtures.					When tested.						Water absorption in per cent of dry-weight brick.
	Parts coarse sand.	Parts fine sand including impurities.	Per cent kaolin.	Per cent quicklime.		At once after hardening.		After aging.		After freezing.		
				Pure CaO.	Dolomite.	Crushing strength.	Tensile strength.	Crushing strength.	Tensile strength.	Crushing strength.	Tensile strength.	
85	4	1	2.5	5	2,766	338	2,449	194	2,917	219	8.32
86	4	1	5.0	5	2,500	210	2,376	277	2,481	181	8.00
87	4	1	10.0	5	1,943	184	1,687	157	1,910	121	8.50
88	4	1	20.0	5	1,705	162	1,325	138	1,477	93	9.00
83	3	2	5	3,697	427	3,812	215	8.06
89	3	2	5	2,260	238	1,846	187	2,117	156	10.36
93	4	1	2.5	5	3,835	351	3,955	364	4,502	352	8.62
94	4	1	5.0	5	3,340	295	3,342	175	3,887	269	8.60
89	3	2	5	2,260	238	1,846	187	2,117	156
92	3	2	20	4,729	599	3,780	596	5,957	480
83	3	2	5	3,697	427	3,812
90	3	2	10	5,607	503	5,843	446	7,525	417
A ¹	2	1	10	7,745	437	9,007	371	8.62
C ²	2	1	10	10	5,872	593	6,194	561	6.41
B ³	2	1	10	5,187	286	5,853	314	9.11
D ⁴	2	1	10	10	4,429	445	4,818	459	8.05

The effect of feldspar as one of the impurities in sand was also studied, but not with the same degree of fullness as was that of clay. The results are shown in the following table:

¹ A is the average of tests number 106, 107, 108, 109, 110 and 111.² C is the average of tests number 118, 119 and 120.³ B is the average of tests number 112, 113, 114, 115, 116 and 117.⁴ D is the average of tests number 121, 122 and 123.

TABLE 18—*Effect of feldspar in sand-lime brick mixtures.*

(By S. V. Peppel)

Data:

Steam pressure—150 pounds per square inch.

Temperature in hardening cylinder—185° C.

Time exposed to steam—10 hours.

Molding pressure—15,000 pounds per square inch.

Number of tests.	Composition of mixture.					When tested.						Water absorption in per cent of weight of dry brick.
	Parts coarse sand.	Parts fine sand (including impurities).	Per cent feldspar.	Per cent quicklime.		At once after hardening.		After aging.		After freezing.		
				Pure CaO.	Dolomite.	Crushing strength.	Tensile strength.	Crushing strength.	Tensile strength.	Crushing strength.	Tensile strength.	
B ¹	2	1	0	10	5,187	286	5,853	314	9.11
F ²	2	1	10	10	4,619	339	5,115	197	6.94

The effect of replacing sand with feldspar to the extent of 10 per cent is not to diminish the strength of the brick. Although there is a slight decrease in its crushing strength there is an increase in its tensile strength.

It has been generally supposed that lime and feldspar would not react when mixed and steamed after the manner of hardening sand-lime bricks, but some recent work in the chemical laboratory of the University of Illinois appears to give evidence to the contrary; but whether these two substances react or not is of very little consequence to the sand-lime brick industry, as feldspar is seldom found in sand in sufficient quantities to be detrimental.

Raw clay, when mixed with lime and steamed, will not react with it as quartz does. If, however, the clay be calcined to 500°C. and pulverized and then mixed with slaked lime, the two will unite forming a sort of cement. This fact is made use of in the manufacture of low-grade cements from calcined clay and lime. If the calcination of the clay be carried to 900°, instead of 500°, the mixtures with lime will not set, but they may be hardened by the action of steam. This fact was brought out by J. M. Knot³ in a recent paper before the American Ceramic Society in Pittsburg. It would thus seem that sands containing large amounts of clay might be rendered suitable for the manufacture of sand-lime bricks by being subjected to preliminary roasting.

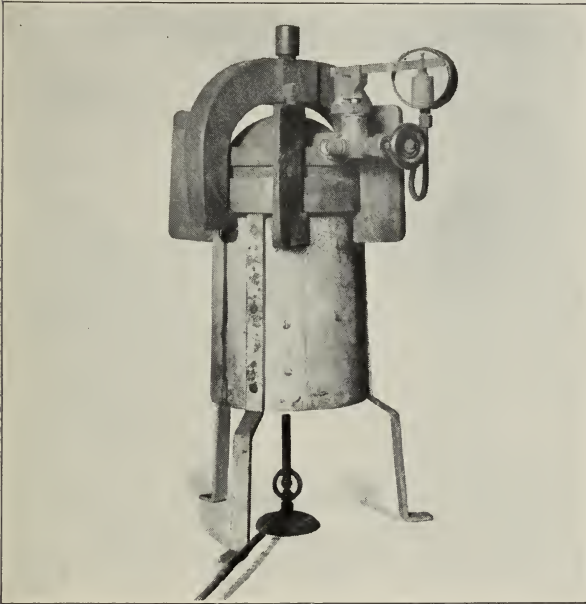
PRESSURE IN MOLDING BRICKS.

The object to be accomplished in pressing mixtures in brick making is not only to shape the mass and give it sufficient strength to stand up in the hardening cylinder, but also to bring the reacting materials into

¹ B is the average of tests number 112, 113, 114, 115, 116, and 117.

² F is the average tests number 124, 125 and 126.

³ Proc. Am. Ceramic Society, vol. 12, 1910, p. 233.



Apparatus used for hardening mixtures of lime and silica by steam.

close enough contact so that chemical reaction can take place. The ideal condition is reached when the sand grains are pressed closely together with only a film of lime between them. The most economic pressure to use in any case will vary, it would seem, with the character of the mixture. Peppel finds that the best results are obtained when 15,000 pounds pressure is applied for each square inch of surface, and that pressures higher than this produce bricks of lower crushing strength. This is a question of very great importance, for, while it seems improbable that pressure too great for the good of the brick is likely to be employed, nevertheless there is a limit beyond which it is poor economy to carry it, because of possible evil effects on the mold liners.

The character of the sand grains has much to do with the matter of pressing, for, while the same pressure was used in molding all the mixtures studied by the authors, those mixtures containing round sand grains produced bricks with the lower absorption. This can be accounted for only by supposing that the round grains move on one another more rapidly, pack more closely and leave less room between them than do sharp grains.

If the material to be pressed is very fine, presses must be constructed so as to allow air to escape. This is accomplished in some presses by causing the die first to descend, then to rise a little, and finally to descend again for the final compression. By this procedure any air which is unable to escape during the first plunge of the die and which might rupture the brick if allowed to remain, escapes when the die is raised.

HARDENING BRICKS.

It is very essential that the cylinder used in hardening the bricks be well constructed, for weaknesses in this part of the equipment are dangerous. The usual practice is to steam for 10 hours at 120 pounds pressure per square inch. Some experiments were undertaken by Peppel for the purpose of determining the best condition under which hardening should be accomplished. His results are quoted below:

TABLE 19—*Effect of time and pressure in hardening process upon the quality of sand-lime brick.*

(By S. V. Peppel)

Steam pressure, 150 pounds.

Hours in steam.	A.		B.		C.		D.		E.	
	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²
4.....	7,896	544	5,303	392	5,282	591	4,514	470	4,441	330
6.....	7,994	390	5,045	199
8.....	7,404	509	4,957	262	6,170	632	4,249	430	4,491	337
10.....	7,767	464	4,902	284
12.....	7,514	337	5,064	250	6,165	556	4,543	434	4,924	349
14.....	7,894	380	5,849	329

Steam pressure, 120 pounds.

Hours in steam.	A.		B.		C.		D.		E.	
	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²
4.....	6,989	5,989	5,403	4,300	5,760
6.....	7,063	6,495
8.....	8,545	6,038	5,868	5,142	6,718

Steam pressure, 100 pounds.

Hours in steam.	A.		B.		C.		D.		E.	
	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²	C. S. ¹	T. S. ²
4.....	6,385	5,921	4,280	4,048	4,588
8.....	7,566	6,507	5,564	4,456	6,544
12.....	7,494	5,753

The conclusion deduced from this work is that four hours at 150 pounds steam pressure is sufficient to make good bricks; that from six to eight hours are required at 120 pounds; and from eight to 12 hours at 100 pounds.

¹ C. S. is crushing strength, lbs. per square inch.

² T. S. is tensile strength, lbs. per square inch.

THE CHEMISTRY OF SAND-LIME BRICKS.

REVIEW OF PREVIOUS WORK.

The literature of sand-lime bricks is not very extensive, and that which has appeared, with few exceptions, has dealt only with the technology of the subject. It has been known from the very beginning of the industry that the bond in sand-lime bricks is a hydrated calcium silicate. This was an easy matter to determine, for it was known that if pure lime and pure silica produce a bond a calcium silicate must be formed. Furthermore, it was easy to determine that when lime is steamed with quartz it renders some of the silica soluble, and that in the product a certain amount of water is held in chemical combination. Further than this no satisfactory evidence as to the composition and properties of the bond of sand-lime bricks has appeared. Its nature, therefore, is largely an unsolved problem.

The hypothesis has been advanced that the bond of a sand-lime brick resembles very closely some of the calcium silicates in set Portland cement. This assumption appears to be quite plausible, inasmuch as the calcium silicates found in set Portland cement are formed by the combination of the calcium hydroxide and silicic acid resulting from the hydrolysis of the ground clinker. But whether this is true or not, it is merely conjecture, and there is no direct evidence either for or against the assumption.

An article by George F. Ransom,¹ devoted to a discussion of the chemistry of sand-lime bricks appeared several years ago. In this the writer shows that a change takes place in the nature of a sand-lime brick during the hardening processes, and that this change can not be physical, and, consequently, must be chemical in its nature. In the latter part of his article, the author develops the fact that a hydrated calcium silicate must be formed. His conclusion is quoted:

"Therefore, I claim that a chemical change does take place during the steaming, and that the bonding material is calcium hydrosilicate."

This article is only a verification of the claims made in the original Michaelis patent, and in reality adds nothing to our knowledge of the chemistry of the bonding material.

In a recent issue of the *Mineral Resources of the United States* Edwin C. Eckel² states that chemical methods are of no value in determining

¹ *Rock Products*, vol. 7, 1907, p. 49.

² *Mineral Resources of the United States*, 1906, U. S. Geol. Survey, Washington, 1907, p. 991.

the nature of the bond in sand-lime bricks, and that only those processes involving the use of the petrographic microscope give any promise of success in the solution of the problem. He accordingly submitted specimens of sand-lime bricks for examination to Frederick E. Wright of the Geophysical Laboratory of the Carnegie Institution, with the following results:

"Mr. Wright states that the binding material of these specimens is a hydrous lime silicate somewhat akin to the familiar minerals of the zeolite group. The reactions involved in the formation of such hydrous silicate, from lime and sand in the presence of steam, are simple and well known. It is to be noted, however, that these reactions are in no way comparable to those which take place during Portland-cement manufacture and that the binding material of sand-lime brick is very different in composition and relationship from Portland-cement clinker.

It may safely be assumed, then, that a sand-lime brick as marketed consists of (1) sand grains held together by a network of (2) hydrous lime silicate, with probably (if a magnesian lime were used) some allied magnesium silicate, and (3) lime hydrate or a mixture of lime and magnesia hydrates. These three elements will always be present, and the structural value of the brick will depend in large part on the relative percentages in which the sand, the silicates, and the hydrates occur."

Mr. Eckel appears to be convinced that the bonding material of sand-lime brick is a very different thing from the calcium silicates found in Portland-cement clinker. But Portland-cement clinker is also a very different thing from the set cement, and certainly no one familiar with the processes of manufacture of both sand-lime brick and Portland-cement would attempt to defend the proposition that these two substances have very much in common. There is good reason, however, for supposing that some of the silicates in the set cement are identical with those to be found in the bonding material of sand-lime brick, and petrographic or any other evidence on the subject would be quite welcome indeed. A brief discussion as to the availability of the petrographic microscope for research on this subject will be taken up later.

Notwithstanding the conclusion of Mr. Eckel, it was still thought that chemical methods might give some valuable information on this very interesting subject. Work was accordingly begun on this problem in the fall of the year 1907, and pursued to some extent throughout the year. The fine-grained silica from Southern Illinois was used in part as the silicious component of the mixture, and the results of the investigation were embodied in a thesis submitted to the chemical faculty of the University of Illinois as a part of the requirements for the degree of master of arts in June of the following year.

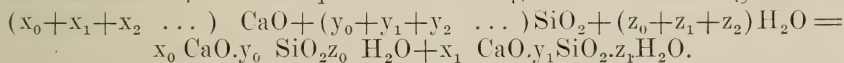
In working with the finely divided silica it was found that by mixing it intimately with lime in equal proportions, pressing, and steaming, a reaction was brought about that resulted in the formation of a nearly homogeneous calcium silicate. This was supposed to be very nearly the same as the bonding material of sand-lime bricks, and a study of it was therefore undertaken. By determining the free and combined lime and

the combined silica in the product it was possible to find approximately the proportions in which these materials react. As a result of a number of analyses, it was learned that the reaction was most complete when the lime and silica were employed in equal quantities. Bricks made from lime and silica also showed greatest strength when the percentages of lime and silica used in the mixture were about equal. This led to the conclusion that the formula for the calcium silicate in the bond of the bricks is $\text{CaSiO}_3 \cdot x(\text{H}_2\text{O})$. Determinations of the combined water seemed to indicate also that one molecule of water was combined with one of lime and one of silica, and the opinion was advanced that $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ was the most probable formula of the compound.

CHEMICAL INVESTIGATION.

THEORETICAL.

When mixtures of lime and silica are subjected to the action of saturated steam at various temperatures combination takes place with the formation of one or more hydrous calcium silicates. The proportions in which these constituents combine are not known, so that to express the reaction requires an equation something like the following:



It might be supposed that the compounds formed are comparatively simple and that the lime-silica ratio in the products of the reaction might in some way be influenced by the proportions in which the lime and silica are present in the uncombined condition, as is the case with silicates formed by fusion. And, furthermore, with a given lime-silica ratio, we would expect that only one compound would exist in equilibrium with water vapor at a series of temperatures and pressures corresponding to those of saturated steam, i. e., the one possessing the highest vapor pressure. For if a calcium silicate having a lower vapor pressure were present under these conditions, it would take up water and pass into the phase with higher vapor pressure. Furthermore, the vapor pressure of any such silicates formed must be lower than the pressure of saturated steam at any definite temperature, for if it were higher it would lose water and revert to a phase with lower vapor pressure. Furthermore, the vapor pressure of any such silicates formed must be lower than the pressure of saturated steam at any definite temperature, for if it were higher it would lose water and revert to a phase with lower vapor pressure.

By the help of the phase rule we are enabled to show this to be true. If we assume the simplest case—that from lime and silica, calcium silicate is formed reversibly, thus: $\text{CaO} + \text{SiO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ —we will have as components, CaO , SiO_2 , and H_2O , while the phases will be water vapor, $\text{Ca}(\text{OH})_2$, SiO_2 , and the compound $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$. The following relation must hold true:

$$P + F = C + 2.$$

in which P =phases, F =degrees of freedom, and C =components. Substituting in this formula and solving for F we have $F=1$. This means that there is but one independent variable (temperature or pressure), or, that a definite temperature necessitates a corresponding definite pressure of water vapor from the compound. A system in which two compounds of the form $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ would be in equilibrium with aqueous vapor would be an invariant one, obtainable at a single temperature and pressure only. Since the products of the union of lime and silica under the conditions of manufacture of sand-lime bricks are stable over quite a range of temperature under the pressure of saturated steam, it is evident that there can be present but one hydrate for each lime-silica ratio used.

We can also examine this reaction as a whole in the light of the phase rule and see what would be possible if the reaction proceeded under equilibrium conditions as represented in the general equation shown above. The number of components is the same as before; namely, CaO , SiO_2 , and H_2O . The reaction is one coming under the reversible class, hence there will always be present some $\text{Ca}(\text{OH})_2$ and SiO_2 , together with water vapor and the solid compound. Now, as before, two solid phases cannot be present in equilibrium except at a single temperature and pressure. It is possible, however, that a compound may be formed under one set of conditions, and because of the slowness with which the reaction proceeds, still exist under other conditions, even when it is not the stable form under these conditions.

If a system composed of lime, silica, and water vapor be in equilibrium at, say, 100° and under one atmosphere pressure, then a change in temperature which would result in raising the pressure to ten atmospheres, if it produced a change in the equilibrium at all, would cause it to shift in the direction corresponding to an absorption of water vapor or an absorption of heat. Both these changes may occur simultaneously, however, or they may occur in opposite directions, in which case the one having greatest effect will be in the direction tending to maintain the original conditions. This means that a compound, stable under the conditions of lower temperature and pressure, might decompose, giving off some or all of its water at the higher pressure, but in this case the heat absorbed would exert a greater influence toward the maintenance of the original conditions than the dissociated water vapor would exert toward destroying them.

In any attempt to determine the chemical composition or formula of a substance, the first consideration is to get it pure, or to work out a method whereby analysis can be carried out in the presence of impurities. In the production of sand-lime bricks the reaction is never complete; consequently, there is always a mixture of the original materials together with the compound or compounds formed.

In the pursuit of this work two general methods were followed in the preparation of the material for analyses. In one of these a small percentage of lime was used, and in the other a small percentage of silica. The mass action law teaches that in a reversible reaction the ratio of the products of the concentration (raised to powers corresponding to

the number of parts entering into the reaction) of the constituents on each side of the equation is a constant, and this holds at least qualitatively for all chemical reactions. Thus, by increasing the amount of lime used in a mixture and using only a small amount of very finely divided silica, it is safe to assume that practically all the silica will enter into combination. If this be true, the first step in the solution of the problem is to remove the uncombined lime without decomposing the calcium silicate. Another method of attack consists in using only a small amount of lime with quartz of such size that it will be readily attacked by the lime, but not so small that it will be appreciably soluble in dilute alkalies. Both these methods were used in these experiments.

PREPARATION OF MATERIALS FOR ANALYSIS.

The lime used in the preparation of the compounds to be analyzed was Kahlbaum's best calcium oxide, burned from pure marble. It was slaked in a beaker placed in a desiccator over sticks of caustic potash. The slaking was done by placing another beaker containing water in the desiccator with the lime and exhausting the air. As the water evaporated, it combined with the lime which crumbled to a powder and was afterward sifted out from any remaining lumps and kept in a desiccator over caustic potash.

The finely divided silica was prepared by precipitating silicic acid from sodium silicate by the use of hydrochloric acid, evaporating to dryness and washing out the sodium chloride. By this process a very fine, pure product was obtained which was kept in a bottle for use.

Two grades of sand were prepared by grinding crushed quartz and standard Ottawa sand. The material was run through a disk pulverizer. The coarse and the very fine material were removed and that which passed an 80-mesh sieve and was retained on a 120 was kept. The two portions saved were washed first in hydrochloric acid, then in chromic acid, then in a solution of caustic soda, and finally in dilute hydrochloric acid and water. When dry the two sands were again carefully screened and placed in suitable containers.

For this phase of the work, samples were not made by pressure, but were merely mixed up in the proper proportions and steamed in suitable vessels. The apparatus used for hardening was the small autoclave shown in plate IV, fitted with a gauge reading kilograms per square centimeter. It was capable of withstanding a pressure of about 25 atmospheres per square inch.

Samples for analysis were prepared by weighing out the proper amounts of lime and sand or silica, mixing in the dry condition, and then adding water which had previously been boiled to expel carbon dioxide, and again mixing. When properly blended, the crucibles or dishes were placed in the autoclave, in which the water was already boiling, so that all carbon dioxide was excluded, the lid was fastened down and the steam pressure was brought up as quickly as possible. When large amounts of material were to be prepared a silver dish holding about 200 cc. was used, but in some cases the mixtures were made

in platinum crucibles. Samples prepared from fine sand and low percentages of lime, when treated with phenolphthalein, reacted slowly, thus showing that the free lime had practically all combined with the silica. In samples in which an excess of lime was used with precipitated silica there was always free lime in the product. After making several inefficient attempts to remove the lime by washing with water, an attempt was made to remove it with the aid of dilute acetic acid. After preparing the compound it was placed in a beaker with boiled water. A few drops of phenolphthalein were introduced and dilute acetic acid added until the color of the liquid just disappeared. Upon the recurrence of the color more acid was added, and this procedure was repeated until the color reappeared very slowly. It was found that even dilute acetic acid had the power to decompose hydrated lime silicates. However, by working very carefully, it was possible to remove small amounts of lime without appreciable decomposition of the silicates. This method was then combined with another in which the preparation was placed in a large beaker and thoroughly agitated by a whirling motion. The lime hydrate being flocculent remained in suspension longer than the silicate and could be siphoned off. The final washing was with dilute acid, as before.

Since acetic was too strong an acid to be used conveniently in this separation, a weaker one was sought. The ionization constants of some of the weaker acids are as follows:

TABLE 20—*Ionization constants¹ at 18°.*

Boric.....	$\text{H}_2\text{BO}_3^- + \text{H}^+ \dots$	1.7×10^{-9}
Hydrosulphide.....	$\text{S}^{--} + \text{H}^+ \dots$	1.2×10^{-15}
Hydrosulphic.....	$\text{HS}^- + \text{H}^+ \dots$	9.1×10^{-8}
Hydrocarbonate.....	$\text{CO}_3^{--} + \text{H}^+ \dots$	6.0×10^{-11}
Carbonic.....	$\text{HCO}_3^- + \text{H}^+ \dots$	3.0×10^{-7}
Acetic.....	$\text{C}_2\text{H}_3\text{O}_2^- + \text{H}^+ \dots$	1.8×10^{-5}
Phenol ²	$\text{C}_6\text{H}_5\text{O}^- + \text{H}^+ \dots$	1.3×10^{-10}

It is essential that the substance used for removing free lime from mixtures of lime and calcium silicate be not only inactive on the silicate, but that it form a soluble compound with lime. Both phenol and hydrogen sulphide are very weak acids and form soluble compounds with lime. They were both tried and appeared to be without action on the silicates. The silicate stood indefinitely without any apparent decomposition, under a pressure of H_2S as furnished by a Kipp gas generator, and all the lime was completely washed from the mixture without difficulty. This acid was therefore chosen as the means of removing the lime from the samples before analysis.

The action of carbonic acid on the mixture of lime and calcium silicate was also studied, and the conclusion was reached that the silicate is

¹ Jour. Am. Chem. Soc., vol. 31, 1909, p. 760.

² Zeitschrift physik. Chem., vol. 32, 1900, p. 137.

completely decomposed by the action of this gas, with the formation of calcium carbonate and free silicic acid. Carbonic acid has also the power to throw down calcium carbonate from solutions of calcium sulphide with the formation of the corresponding acid; consequently, it was necessary to exclude it when purifying the silicate.

METHODS OF ANALYSIS.

Samples made up with an excess of lime were first freed of lime, after which analysis was carried out in the usual way. The silica was determined by treating with hydrochloric acid and evaporating to dryness several times. In the filtrate from the silica the lime was determined by precipitating as the oxalate, washing and titrating with potassium permanganate. The permanganate solution was standardized against a calcium solution of known strength in the same way that it was used in the determinations, so that any small errors inherent in the method would cancel.

In samples made up with excess of fine sand, the soluble silica had to be separated from the unattacked quartz. The work of Lunge and Millberg¹ shows conclusively that in order to make this separation quantitative the quartz grains must be of a size such that they will settle out of water quickly. With "dust fine" quartz powder a two-hour digestion on the water bath with a 1 per cent solution of sodium carbonate dissolved 2.10 per cent of the weight of quartz taken. With a 15 per cent solution of either sodium or potassium carbonate, on the other hand, only a very slight trace of quartz was dissolved by a two-hours' digestion when the grains were large enough to settle out of water readily. Hydrated silicates such as trass, opal, pozzuolan, etc. dissolved almost completely with the same treatment.

It might be supposed that silicates of the sort here studied would dissolve completely in acid, but the separation of combined silica is not so easily effected. On the addition of a strong acid the silicate is decomposed, the calcium going into solution as a salt of the corresponding acid, with part of the silicic acid precipitating as a colloid and the balance remaining in solution. The quantity which will stay in solution will depend very largely on the concentration of the acid used. A strong acid will precipitate much of the silica while a very dilute acid will precipitate but a very small part of it. Hence the necessity of following any acid treatment with an alkaline solvent under such conditions that the separated silica may be redissolved while the quartz particles are unattacked.

Our determinations were made by first crushing the sample to be analyzed in a manner not to further reduce the size of the sand particles. It was then treated in a casserole with 250 cc. of a solution of hydrochloric acid, made by diluting the strong acid (1.10 sp. gr.) to ten times its volume with distilled water, and digested on the water bath or over a low flame (so that it would not boil) for several hours, the time depending somewhat on the character of the sample. It is quite

¹ Zeit. angew. Chem., 1897, pp. 393 and 425.

essential that the acid be not too strong, and that the solution be kept from boiling during the digestion, in order that the silicic acid may remain in solution and not interfere with the subsequent filtration.

After the digestion was complete, the solution was filtered off by suction through a reinforced filter. When the digestion had been properly carried out the filtration was easily done, but when the silicic acid separated it was a very difficult process. After filtration, the sand was treated with a few cubic centimeters of water and washed by decantation. The filter was then placed in the casserole and 100 cc. of water added. Five grams of sodium carbonate were then weighed out roughly and added to the water in the casserole and digestion carried out as before for about an hour, after which the solution was again filtered off. If very accurate work is to be done this digestion with a 5 per cent solution of sodium carbonate should be repeated. Little difficulty from clogging of the filter is experienced with these later filtrations.

After the separation is complete the filter papers may be burned and weighed. The soluble silica is determined in the filtrate by evaporating the combined solutions to dryness on the water bath in the ordinary way, two evaporations being usually sufficient for this work. The lime is determined in the filtrate as before.

When free lime is found in the sample it is necessary to remove this, or to determine the amount present, before proceeding with the silica determination. It can be removed by treating with hydrogen sulphide, which converts the free calcium hydrate to the sulphide or acid sulphide, in which form it is soluble and can be washed out. Care should be taken to use water from which the carbon dioxide has been removed by boiling, for, otherwise, calcium carbonate will be precipitated and will cause error. In case the free lime is to be determined, this can be done by allowing the material to stand in a closed flask with distilled water, which with occasional shaking will dissolve the lime, when an aliquot part can be drawn off and the lime titrated with standard acid. If there is very much free lime the sample taken should be small, or some sugar should be added to the water, to make sure that all the lime present dissolves. Other methods might be used in special cases, but these appear to be very satisfactory for all ordinary determinations.

RESULTS OF CHEMICAL ANALYSES.

SILICATE NO. 1.

This sample was made with three parts of lime to one of precipitated silica. Steaming was at 12-15 atmospheres per square inch for 10 hours, and excess lime was removed, first, by decantation of the flocculent hydrate, and, then, by treatment with phenolphthalein and dilute acetic acid.

The lime-silica ratio as determined was .674/1, which is rather high for silica owing to the fact that some of the silicate was decomposed by the action of the acetic acid.

SILICATE NO. 2.

This sample was made by mixing three parts of the sand prepared from crushed quartz with one part of lime hydrate. The steaming was at 12-15 atmospheres per square inch for 8 hours. Excess lime was removed by treatment with dilute acetic acid.

Lime-silica ratio=.899/1.

SILICATE NO. 3.

This sample was made in substantially the same way as Sample No. 2.

Lime-silica ratio=.870/1.

SILICATE NO. 4.

This sample was made with 10 per cent of CaO and the same crushed quartz. It was steamed 8 hours at 12-15 atmospheres. The lime was washed out with acetic acid.

Lime-silica ratio=.863/1.

Water-silica ratio=.632/1.

Calculated chemical formula= $9\text{CaO} \cdot \text{SiO}_2 \cdot 6\text{H}_2\text{O}$.

SILICATE NO. 5.

This sample was made with 15 per cent CaO and fine quartz sand. Steaming was for 8 hours at 15 atmospheres. The excess of lime was removed by boiling with additions of a solution of ferric chloride. This caused the precipitation of ferric hydroxide, which, being flocculent, could be siphoned off with the supernatant liquid. This process was carried on until the clear liquid showed no color with phenolphthalein. The analysis was carried out as usual, except that the iron had to be removed before determining calcium.

Lime-silica ratio=.890/1.

Water-silica ratio=.508/1.

Calculated chemical formula= $9\text{CaO} \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$.

SILICATE NO. 6.

This sample was made with three parts of CaO to one of precipitated silica. The ingredients were mixed with water to the consistency of a thick cream or slurry and steamed for 8 hours at 12-15 atmospheres. The excess lime was removed by agitating and decanting flocculent lime hydrate, and, finally, by addition of acetic acid and phenolphthalein and washing.

Lime-silica ratio=.847/1.

SILICATE NO. 7.

This sample was made with 10 per cent CaO and the fine crushed quartz sand used before, steamed for 8 hours at 15 atmospheres. The lime was practically all combined.

Lime-silica ratio=.818/1.

SILICATE NO. 8.

This sample was made with 3.75 per cent CaO and fine crushed quartz. Steamed for 8 hours at 12-15 atmospheres.

Lime-silica ratio = .873/1.

Water-silica ratio = .726/1.

Calculated chemical formula = $8\text{CaO} \cdot \text{SiO}_2 \cdot 7\text{H}_2\text{O}$.

SILICATE NO. 9.

This sample was made with 7.5 per cent of CaO and the fine crushed quartz. It was steamed, as before, at 12-15 atmospheres. After steaming only a trace of free lime was left.

Lime-silica ratio = .837/1.

Water-silica ratio = .837/1.

Calculated chemical formula = $8\text{CaO} \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O}$.

SILICATE NO. 10.

This sample was made by using 8.75 per cent CaO with the crushed quartz. It was steamed as before at 12-15 atmospheres. The free lime found after steaming was negligible.

Lime-silica ratio = .853/1.

Water-silica ratio = .824/1.

Calculated chemical formula = $9\text{CaO} \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O}$.

During the hardening of this sample, water collected above the material in the dish and on this a crust was formed. The crust dissolved completely in dilute hydrochloric acid and showed a lime-silica ratio of .968/1.

SILICATE NO. 11.

This sample was made by using 15 per cent of lime with fine quartz sand. The free lime was removed by precipitating with Fe_2Cl_6 and decanting flocculent ferric hydrate. The sample was dried at 101° , and separated into two parts (a fine and a coarse) by means of sieves. Analysis showed the following results:

Coarse Part.

Fine Part.

Lime-silica ratio = .910/1.

Lime-silica ratio = .833/1.

Water-silica ratio = .544/1.

Calculated chemical formula = $9\text{CaO} \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$.

SILICATE NO. 12.

Silicate No. 12 was made with 7.5 per cent CaO and the fine sand prepared from Ottawa Standard sand. The steaming conditions were the same as before, 12-15 atmospheres for 8 hours.

Lime-silica ratio = .887/1.

Water-silica ratio = .748/1.

Calculated chemical formula = $8\text{CaO} \cdot \text{SiO}_2 \cdot 7\text{H}_2\text{O}$.

A portion of this sample was ground with a soft pestle in a mortar so as to remove the binding material from the sand grains as much as possible. The part passing an 80-mesh sieve and retained on one of 120 meshes was subjected to a process of fractionation in a separating funnel originally devised by Harada¹ for the separation of minerals. Thoulet's² solution was used for the separation and three fractions were taken. Analyses of the heavy and light fractions gave these results:

Lime-silicate ratio of heavy fraction=.885/1.

Lime-silicate ratio of light fraction =.830/1.

SILICATE NO. 13.

This sample was made with 10 per cent CaO and the fine sand from crushed quartz. It was steamed for 8 hours at 12-15 atmospheres, dried at 101°, and then ground as before with a soft pestle in a mortar. The part passing a 120-mesh and retained on one of 200 meshes was retained and fractioned with the aid of the Thoulet's solution. Four fractions were analyzed. These yielded the results recorded in the following table:

TABLE 21—*Analyses of fractions separated from lime-silicate.*

Fraction.	Sand— Per cent.	Soluble SiO ₂ — Per cent.	Lime— Per cent.	Lime-silica ratio.
1.....	55.75	21.75	22.57	1.11 : 1
2.....	56.70	21.95	21.40	1.04 : 1
3.....	34.65	32.75	32.60	1.08 : 1
4.....	1.24	50.00	48.76	1.04 : 1

SILICATE NO. 14.

This sample was made by using three parts of CaO to one of precipitated silica, mixing with enough water to form a slurry, shaking well, and steaming for 8 hours at 15-20 atmospheres. The steamed mass was washed with boiled water into a liter flask, some phenolphthalein added and the flask then connected to a source of hydrogen sulphide. This gas combined with the lime and formed a soluble sulphide which was removed several times by decantation. The process was continued until there was hardly any reaction with phenolphthalein. The lime-silica ratios found were:

First fraction (heavy)..... 1.30/1.

Second fraction (heavy)..... 1.11/1.

Third fraction (light)..... 1.13/1.

The following experiments were undertaken for the purpose of ascertaining whether there was any more silica rendered soluble by a given amount of lime when used with crushed quartz than when used with the Ottawa Standard sand.

¹ Neues Jahrbuch für Mineralogie, 1881, I, p. 457.

² Idem, p. 179.

EXPERIMENT NO. 15.

Into each of four platinum crucibles were weighed exactly 0.5 gram of CaO , which was ignited over the blast lamp to remove any traces of CO_2 that might have combined with it. While still hot, 5gr. of Ottawa sand were added to two of these crucibles, and five grams of the sand prepared from the crushed quartz to each of the other two. After cooling, boiling water was added and the lime and sand were thoroughly mixed. The lids were then placed on the crucibles and they were placed on a porcelain desiccator tray in the autoclave, the water in which was boiling so that all air was excluded. Steaming was continued for 8 hours at about 20 atmospheres. Practically all the lime was in combination at the end of the operation. Two of these samples were used in the determination of soluble silica, the other two being used for the determination of combined water. The results of the analyses of the products are shown in the table:

TABLE 22—*Ratios of products of Experiment No. 15.*

	Standard Ottawa sand.	Crushed quartz sand.
Lime-silica ratio.....	1.18 : 1	1.15 : 1
Water-silica ratio.....	.718 : 1	.764 : 1
Calculated chemical formula.....	$1.2\text{CaO} \cdot \text{SiO}_2 \cdot 7\text{H}_2\text{O}$	$1.2\text{CaO} \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O}$

EXPERIMENT NO. 16.

The results shown in the following table are from an experiment exactly parallel to No. 15, except that the amount of lime used was one-fourth instead of one-half gram.

TABLE 23—*Ratios of products of Experiment No. 16.*

	Standard Ottawa sand.	Crushed quartz sand.
Lime-silica ratio.....	1.14 : 1	1.11 : 1
Water-silica ratio.....	.689 : 1	.709 : 1
Calculated chemical formula.....	$1.1\text{CaO} \cdot \text{SiO}_2 \cdot 7\text{H}_2\text{O}$	$1.1\text{CaO} \cdot \text{SiO}_2 \cdot 7\text{H}_2\text{O}$

EXPERIMENT NO. 17.

The results shown in the next table are those of an experiment which differed from the one just preceding only in that the steam pressure was 10 atmospheres instead of 20.

TABLE 24—*Ratios of products of Experiment No. 17.*

	Standard Ottawa sand.	Crushed quartz sand.
Lime-silica ratio	1.09 : 1	1.18 : 1
Water-silica ratio897 : 1	1.15 : 1
Calculated chemical formula.....	1.1CaO.SiO ₂ .9H ₂ O	1.2CaO.SiO ₂ .2H ₂ O

TABLE 25—*Summary of results of chemical analyses of lime silicates experimentally produced.*

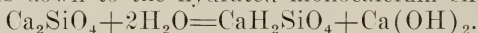
No.	Composition of mixture (approx.).	Experiment number.	Steam pressure in atmospheres used in making product.	Composition of product.			Remarks.
				Mols. CaO.	Mols. SiO ₂ .	Mols. H ₂ O.	
1	CaO.9SiO ₂	4	12-15	0.863	1	0.632
2	CaO.19SiO ₂	5	12-15	0.890	1	0.508
3	CaO.27SiO ₂	8	12-15	0.873	1	0.725
4	CaO.13SiO ₂	9	12-15	0.837	1	0.837
5	CaO.27SiO ₂	10	12-15	0.953	1	0.324
6	CaO.6SiO ₂	11	12-15	0.910	1	0.544
7	CaO.13SiO ₂	12	12-15	0.837	1	0.748
8	CaO.9SiO ₂	15a	19-21	1.18	1	0.718
9	CaO.9SiO ₂	15b	19-21	1.15	1	0.764
10	CaO.19SiO ₂	16a	19-21	1.14	1	0.689
11	CaO.19SiO ₂	16b	19-21	1.11	1	0.709
12	CaO.19SiO ₂	17a	9-11	1.09	1	0.897
13	CaO.19SiO ₂	17b	9-11	1.18	1	1.15
14	CaO.3SiO ₂	2	12-15	0.899	1
15	CaO.3SiO ₂	3	12-15	0.870	1
16	3CaO.SiO ₂	6	12-15	0.847	1	Acetic acid used.....
17	CaO.9SiO ₂	7	12-15	0.818	1
18	CaO.27SiO ₂	10a	12-15	0.968	1
19	CaO.6SiO ₂	11a	12-15	0.833	1
20	CaO.13SiO ₂	121	12-15	0.885	1
21	CaO.13SiO ₂	122	12-15	0.839	1
22	CaO.9SiO ₂	131	12-15	1.11	1
23	CaO.9SiO ₂	132	12-15	1.04	1
24	CaO.9SiO ₂	133	12-15	1.08	1
25	CaO.9SiO ₂	134	12-15	1.04	1
26	3CaO.SiO ₂	141	15-20	1.30	1	H ₂ S used to remove CaO.....
27	3CaO.SiO ₂	142	15-20	1.11	1
28	3CaO.SiO ₂	143	15-20	1.13	1

DISCUSSION OF ANALYSES.

Reference to the table will show that in the products made by steaming silica with lime or calcium hydrate the ratios of lime to silica are all in the neighborhood of one. This indicates that in the bonding material of sand-lime brick the lime and silica are present in nearly equal molecular proportions, and that the major part of it is doubtless the hydrated calcium metasilicate (CaSiO₃.H₂O). The variations from the ratio of 1 to 1 in the experimental products, however, are greater than can be attributed to experimental error, hence other silicates must also have been formed. It would seem that with excess of lime the orthosilicate (Ca₂SiO₄) might be formed, and that with an excess of available silica

there would appear a calcium disilicate such as $\text{CaO}(\text{SiO}_2)_2$. However, there is as yet no direct evidence as to the number of compounds that may be produced by the methods employed. If calcium orthosilicate is a possible product, it would be expected when lime and precipitated silica are mixed in the molecular ratio of 3 to 1, as in numbers 16, 26, 27, and 28. The analyses, however, do not indicate its presence. In this connection it must be remembered that in an atmosphere of dry saturated steam it is possible that such a compound may be stable, while when treated with an excess of water, as it is necessary to do in order to remove the free lime, it may be broken down by hydrolysis, especially when the free lime is removed by converting it into the sulphide or acetate.

When excess of silica is used in the mixture, chemical analysis of the product is difficult if not impossible, unless the silica is in the form of quartz grains of sufficient size to be only slightly acted upon by dilute alkalis. In a mixture composed of such sand grains with from 5 to 20 per cent of lime, only the surfaces of the sand grains furnish available silica for the reaction; consequently, different parts of the mixture will have different compositions, and one would expect several compounds to be formed. Now, if a mixture of compounds such as this be treated with a large excess of water to remove free lime, hydrolysis of the compounds begins, and as the dicalcium silicate hydrates most easily it doubtless goes down to the hydrated monocalcium silicate, thus:



This reaction is one that actually occurs in the setting of cement. It is not improbable that an anhydrous dicalcium silicate may be formed to some extent at high steam pressure. If so, when cooled and treated with water it will hydrolyze as shown in the equation. In practically all of the experiments showing lime-silica ratios lower than one the samples were washed with a considerable quantity of water, and in some cases with the addition to the water of a little very dilute acid or hydrogen sulphide gas. In the samples 9 to 13 this was not done, but tests for free lime were made on material just as it came from the steam cylinder.

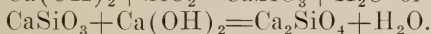
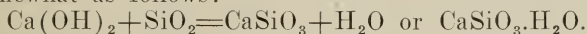
The conclusion seems to be justified that the ratio in which lime and available silica are present in the mixtures will determine to some extent the ratio of lime to silica in the products formed from them. Since the proportion of lime and silica varies in different parts of a sand-lime brick mixture a number of silicates must be present in the bonding material, the greater part of which, however, is doubtless the hydrated metasilicate with some orthosilicate and some disilicate.

In the determination of water the samples were dried to constant weight at 100° , and ignited in the blast flame. The water in combination was found to vary from about a third of a molecule to something more than one molecule to each molecule of silica. It is evidently held with very different degrees of tenacity, and it is quite possible that the amount of water which may be in combination is not constant. It appears to decrease with increasing steam pressures, as shown in experiments Nos. 15, 16, and 17. This must be taken to mean that the

decomposition pressure of some hydrate in the mixture is greater at the higher temperatures employed than the pressure of saturated steam, and, therefore, there is a loss of water at the higher temperatures.

From the facts at hand the conclusion appears to be justified that in sand-lime bricks made from pure calcium lime and silica sand we have a mass of sand grains held together by a bonding material which is a mixture of hydrated calcium silicates. The molecular ratio in which lime and silica occur is nearly equal to unity; consequently, the major portion of this material is doubtless the metasilicate of calcium, hydrated to a greater or less extent. Silicates having a higher and lower calcium-silica ratio than one must be present to a certain extent to account for the variation in this ratio as determined by analysis. The amount of water in combination is evidently quite variable.

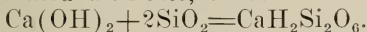
It is probable that under the influence of steam lime is able to attack silica somewhat as follows:



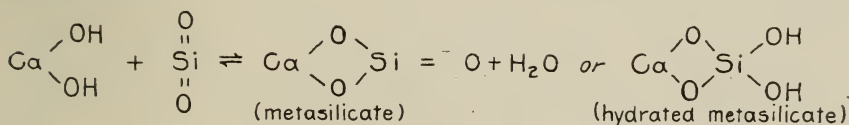
The orthosilicate will doubtless hydrolyze to some extent, as shown in the following equation:



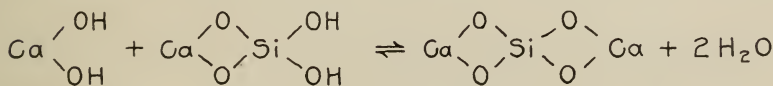
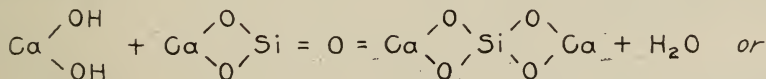
One molecule of lime may also attack two of silica with the formation of an hydrated disilicate, thus:



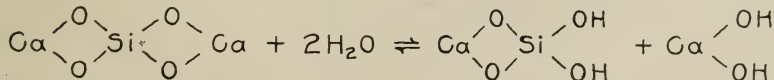
In the light of their structural relations, these reactions appear as follows:



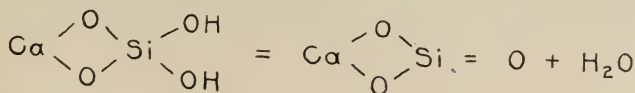
Then again:



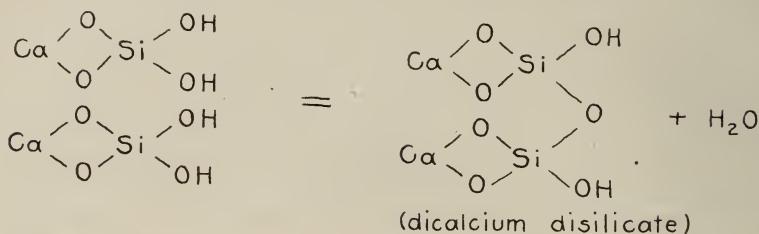
and, by hydrolysis:



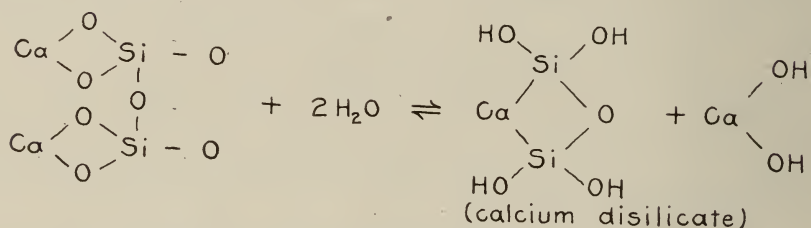
Water may now be eliminated from this to regenerate the anhydrous compound, thus:



Or, two molecules might lose a molecule of water between them, thus giving a double molecule with half the amount of water:



Further, if this double molecule should lose one of its calcium molecules by hydrolysis, a disilicate would result thus:



It is quite probable that all of these reactions take place in the steaming of sand-lime bricks, and perhaps others. The most stable molecules formed are doubtless the simplest ones; consequently, we would expect to find the mass of silicates composed largely of the simple calcium hydro metasilicate. That this is probably the case is shown by the fact that the ratio of combined lime and silica is nearly unity. Varying the ratio of lime to available silica in the raw mixture will have an effect on the relative proportions in which the compounds are formed, as will also a variation in the steam pressure on the relative amounts of water held in combination.

GENERAL CONCLUSIONS AS TO THE CONSTITUTION OF SAND-LIME BRICKS.

1. Sand-lime bricks made from pure materials consist of sand grains cemented together by a bonding substance.
2. Aside from the calcium hydrate or carbonate that may be present, this bonding material consists of a mixture of at least two, and most likely three, calcium silicates, some of which are hydrated.
3. The bulk of this mixture of silicates is calcium metasilicate (CaSiO_3 or $\text{CaSiO}_3 \cdot \text{H}_2\text{O}$).
4. Other silicates which must be present to some extent are calcium orthosilicate and calcium disilicate, the latter of which may contain one or more molecules of water of hydration.

THE PHYSICAL TEXTURE OF SAND-LIME BRICKS.

By the aid of the polarizing microscope, it is possible to distinguish between isotropic and anisotropic media. This may be done for substances very finely divided. Thus, it is an easy matter to distinguish between ground glass and ground quartz or powdered salt and powdered sugar. If the particles are large enough to cover a considerable portion of the field of the microscope, one may distinguish further between uniaxial and biaxial crystals or crystalline substances by observing the interference figures in converged light. This would enable one to say whether the substance crystallizes in either the hexagonal or tetragonal systems, on the one hand, or the orthorhombic, monoclinic or triclinic systems, on the other. If the material should occur in particles large enough, it would be possible to do many other things, but for very small particles it is not possible to say more than that a substance is isotropic or anisotropic, unless definite crystals appear.

In order to gain any light that might be thrown upon the problem in hand by this method of investigation, sections were prepared from several brands of commercial sand-lime bricks, from a small sand-lime brick block made in the laboratory, and from small blocks made from pure silica and lime. Slides were also prepared from material made by heating in sealed tubes, for about a week, mixtures of lime and silica under a pressure of 120 pounds per square inch.

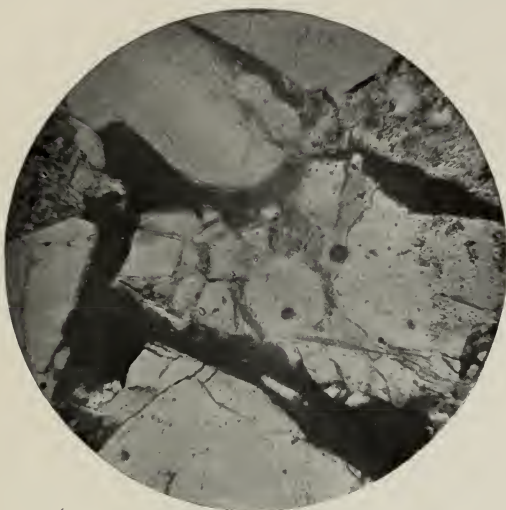
The photomicrographs of sand-lime brick sections shown in Plate V were taken as viewed by polarized light. They show that the bonding material of a sand-lime brick is not transparent like the quartz grains, and, consequently, that if crystalline at all the crystals are very small and closely packed.

Figure A of plate VI is a photomicrograph of a section prepared from equal molecular quantities of pure lime and precipitated silica. The material was thoroughly mixed by grinding in a mortar and then subjected to very great pressure in molding. Two small cylinders one-half inch in diameter were made, and these were steamed in the usual way. The fracture of the material was conchoidal; and the lustre, vitreous. The sections were made as thin as was consistent with the nature of the material. When examined between crossed nicols, the field was uniformly dark except for small spots as shown in figure A. When examined in

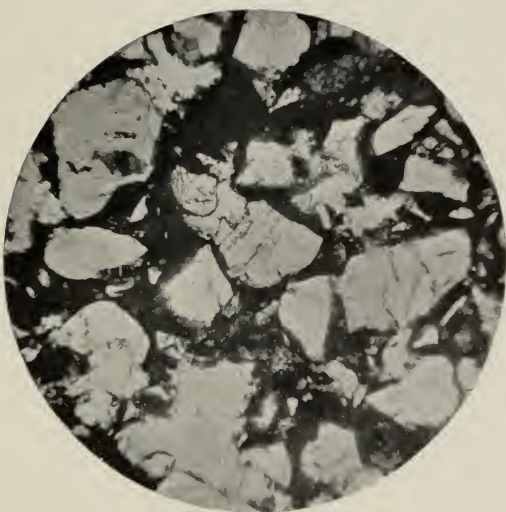
plane polarized light without the use of the upper nicol and at a magnification of 315 diameters the section had the appearance of figure B. The lighter areas are isotropic and evidently must be either a colloid or an aggregate of crystals belonging to the isometric system. The light points which appear between crossed nicols in A are small crystals which are doubly refracting. It was not possible to make further determination of these doubly refracting crystals owing to their small size.

Larger particles of this doubly refracting compound were found in the material prepared as described under silicate No. 14. Some of this after being freed from uncombined lime and washed thoroughly was put into a hard glass tube and sealed. This tube was then left in the steam bath for about two weeks. The material was then removed, washed, dried and mounted in Canada balsam. Somewhat larger crystalline bodies were apparent, but nothing showing a regular outline that would permit of the identification of the crystal system. This slide also furnished particles which in converged light gave the uniaxial interference figure. Calcium hydrate crystallizes in the hexagonal system and so does calcium carbonate, but under the conditions whereby this material was prepared there is hardly a possibility that enough of either of these compounds could be present to form crystals of such size.

It would seem, then, from microscopic evidence that we are warranted in saying that at least two distinct crystalline compounds are present in calcium silicates formed at steam temperatures. The isotropic crystals doubtless represent a compound occurring to some extent in the bonding material of sand-lime bricks, but present in larger amounts in the compounds made from lime and fine silica like that from Southern Illinois. Sections of sand-lime bricks, and in fact all the slides examined, show small, highly doubly refracting crystalline particles that are possibly the zeolitic materials observed by other investigators. The fact that these particles show the uniaxial interference figure indicates that they crystallize either in the hexagonal or in the tetragonal crystal systems.



A



B

Thin sections of sand-lime bricks, viewed in polarized light.
White—quartz grains. Black—bond.

TESTS OF SAND-LIME BRICKS.

The value of a brick for building purposes is determined very largely by the following properties:

A.—Strength:

I. Transverse.

II. Crushing.

B.—Durability:

I. Resistance to weather.

II. Resistance to fire.

C.—Appearance:

I. Character and uniformity of color.

II. Regularity of size, form, etc.

D.—Uniformity of product.

At the last meeting of the American Society for Testing Materials its committee on standard specifications for testing building and paving bricks submitted its report on "Proposed Standard Specifications for Testing Building Brick." Four tests are recognized and the desirability of another (the fire test) is mentioned. The four that were recommended are the transverse test, the compression test, the absorption test and the freezing and thawing test.

The committee recommended that the transverse test be made on the brick placed flatwise on a seven-inch span with the load applied midway between the two supports. The modulus of rupture (R) shall be calcu-

$$\frac{3We}{2bd^2}$$

lated from the formula: $R = \frac{3We}{2bd^2}$ in which W is the load at which the

brick fails, e the distance between supports in inches, and b and d are respectively the breadth and depth of the brick in inches.

The compression test is to be made on a half brick laid flatwise and properly bedded in several thicknesses of blotting paper or felt, or, if very irregular, in plaster of Paris. The ultimate load at which the brick fails divided by the area under compression is taken as the crushing strength in pounds per square inch.

For the absorption test bricks are, first, to be weighed dry, then placed in warm water, removed after one-half hour, wiped dry, and again weighed. This process is to be repeated at intervals of six and forty-eight hours. The absorption is the total gain in weight divided by the weight of the dry brick, recorded in per cents.

For the freezing test the bricks are to be alternately frozen and thawed twenty times, after which they are subjected to the transverse and compression tests.

Sand-lime bricks have been subjected to all the above tests with satisfactory results. It is true that not all sand-lime bricks have been found satisfactory, for many poor bricks have been put on the market, and some of these have found their way to the testing laboratory.

STRENGTH TESTS.

The strength of properly made sand-lime bricks is all that is required by the specifications of the American Society for Testing Materials. As the result of a number of tests, Curfman¹ found the modulus of rupture of sand-lime bricks to be 509, 766, 420, and 607 for four different brands. The results of his crushing tests were as follows:

TABLE 26—*Results of compression tests on sand-lime bricks.*

(By Curfman)

Reference number.	Number tested.	Average ultimate crushing strength in pounds per square inch.
1.....	12	4,344
2.....	3	6,123
3.....	12	2,412
4.....	13	2,244
5.....		7,300
6.....	15 cubes	952
7.....	10	2,943
8.....	1	4,470
9.....	2	3,002
10.....	1	3,147
11.....	3	3,848

Some of these tests were made on bricks that were manufactured when the industry was first introduced into this country and were, consequently, not of as good quality as the bricks now being produced.

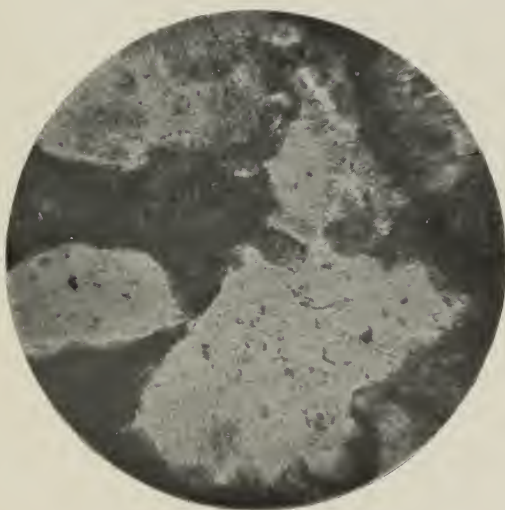
No. 6 was made on cubes and probably ought not be compared with the other tests which were made on half bricks.

Transverse and crushing tests were made by ourselves on 22 samples of each of two brands of commercial sand-lime bricks. The bricks were tested as received and the results are therefore probably considerably lower than they would have been had the brick been dried at 100° before testing. The results obtained are shown in the following table:

¹ Technograph, vol. XIX, 1905, p. 72.



A



B

Microscopic sections of steamed lime-silica mixtures.

TABLE 27—*Tests of sand-lime brick.*

Brand A.			Brand B.		
No.	Modulus of rupture. ¹	Crushing strength in lbs. per square inch.	No.	Modulus of rupture.	Crushing strength in lbs. per square inch.
1.....	435	4,230	1.....	843	4,420
2.....	427	4,340	2.....	952	4,000
3.....	472	4,750	3.....	728	3,980
4.....	484	5,000	4.....	662	2,880
5.....	416	4,040	5.....	675	*2,440
6.....	422	4,340	6.....	605	2,950
7.....	414	3,900	7.....	957	3,800
8.....	*246	*3,800	8.....	700	3,540
9.....	351	4,000	9.....	*635	2,790
10.....	305	3,950	10.....	587	*2,490
11.....	*302	3,900	11.....	653	3,570
12.....	383	4,600	12.....	675	3,460
13.....	405	3,820	13.....	645	2,750
14.....	375	3,960	14.....	572	3,060
15.....	423	4,850	15.....	686	3,620
16.....	475	4,750	16.....		3,020
17.....	432	4,400	17.....	761	3,540
18.....	437	*5,140	18.....	700	2,780
19.....	468	4,130	19.....	806	4,300
20.....	420	4,360	20.....	723	3,900
21.....	460	5,000	21.....	661	3,360
22.....	427	3,980	22.....	743	3,490
Mean.....	420	4,320	Mean.....	720	3,470

EFFECTS OF FREEZING BRICKS.

The ability of any material to withstand the action of the weather will depend very largely on the amount of water it will absorb. If only a little water is taken up (5-10%) this will be held very largely by the capillarity, and it will not segregate to form ice crystals when frozen, while if more water is taken up, freezing will cause ice crystals to form within the body of the brick and wedge its particles apart. Sand-lime bricks can be made with absorption as low as 5 per cent, but this is expensive and undesirable, since about 8 per cent of absorption is needed to dry the mortar used in laying the bricks and make it stick. Brick with 10 per cent absorption can easily be made, and this should be the goal toward which the manufacturer should work. As has been said before, the bonding material in sand-lime brick is the real absorbing constituent; consequently, if the absorption is too high, the quantity of bond made should be reduced by decreasing the ratio of fine or dust-like constituent in the mixture. The following table showing the effect of freezing on brick is quoted from Curfman's article (loc. cit.).

¹ First eleven tests were made on bricks placed edgewise.

* These tests are not included in the means.

TABLE 28—*Effect of freezing on crushing strength and absorption of sand-lime bricks.*

Reference mark.	Private mark.	Number tested.	Absorption—Per cent by weight.		Average crushing strength—Pounds per square inch.		
			Before freezing.	After freezing.	Before freezing.	After freezing.	Loss in weight.
1.....	C.....	4	10.85	14.25	4,448	3,430	Not found
2.....	Cs.....	2	8.80	9.20	6,200	6,225	Not found
3.....	U.....	6	13.16	14.97	2,470	1,778	14.20

It will be noted that the brick which was strongest after freezing was the one possessing the lowest absorption.

FIRE RESISTING QUALITIES OF SAND-LIME BRICKS.

The effect of fire on sand-lime bricks has attracted a great deal of attention, and it is a question of considerable importance. The condition of the walls of a building that has burned is, in some cases, a matter of thousands of dollars. Many investigations have been undertaken for the purpose of studying this property, but most of them have been of a qualitative nature only.

Curfman constructed a small house or kiln of the bricks to be tested, and in this he built a wood fire which was kept burning for a little more than half an hour. The bricks were then removed and tested for soundness by blows with a stick, and for crushing strength. Again in another test, he dashed the previously heated walls with cold water, and studied the effects. In still another experiment he placed several half bricks on the traveling gate of an automatically stoked boiler and allowed them to pass through the fire box. In none of these experiments was any attempt made to determine the temperature to which the bricks were subjected, but it is safe to assume that it was in the neighborhood of 1000° C. in the last experiment. At high temperatures the bond was found to be destroyed.

The effect of fire on a sand-lime brick wall was studied at the Underwriters Laboratory, Chicago, by Richard L. Humphrey,¹ who constructed a furnace having one side closed with a panel built of the material to be tested. Temperatures were carefully measured both inside the furnace and at the back of the wall. During the test made with sand-lime bricks the wall bulged considerably toward the fire. After firing 40 minutes, the faces of the bricks next the fire had a chalky appearance, as though the lime were dehydrated, and when quenched with water after a two-hours fire, the bricks spalled off to an average depth of about half an inch. Some of the bricks were removed from the panel and tested for strength, absorption, etc. The results of these tests are shown in the table below:

¹ Bull. U. S. Geol. Survey, No. 379, 1909, p. 77.

TABLE 29—*Physical properties of sand-lime brick before and after firing.*
(By R. L. Humphrey)

	Normal.		Immersed in water for 48 hours.			Water absorption.		
	Transverse strength.		Com- pressive strength per square inch.	Com- pressive strength per square inch.	Re- duction in com- pressive strength.	30 min- utes.	4 hours.	48 hours.
	Breaking load.	Modulus of rup- ture.						
	<i>Pounds.</i>		<i>Pounds.</i>	<i>Pounds.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Not fired.....	913	364	2,020	1,816	10.1	16.33	16.59	16.59
	909	362	2,510	1,636	34.8	16.30	16.60	16.60
	797	318	2,161	1,604	25.8	9.81	13.62	13.62
	684	273	1,923	1,382	28.1	18.22	18.29	18.29
	695	277	1,562	963	38.3	13.04	13.91	14.28
Average.....	800	319	2,035	1,480	27.4	14.74	15.80	15.88
Brick from back of wall.....	642	256	2,117	1,261	40.5	15.30	15.3	15.3
	841	336	2,109	976	53.7	11.90	13.45	14.00
	770	308	1,208	1,451	*20.0	13.72	15.79	15.79
	789	315	2,430	1,468	39.6	13.80	14.30	14.30
	645	258	1,790	873	52.2	16.92	16.92	16.92
Average.....	737	295	1,931	1,206	33.2	14.33	15.15	15.26
Brick with ends exposed.....	494	197	1,952	1,189	39.1	14.65	14.65	14.65
	756	302	2,176	826	62.0	12.30	13.20	13.20
	707	282	2,109	1,157	45.0	13.90	13.90	13.90
	463	185	1,306	1,444	*10.5	12.00	13.80	13.80
	551	220	1,541	1,289	16.4	10.40	12.87	12.87
Average.....	594	237	1,817	1,181	30.4	12.65	13.68	13.68
Brick with face ex- posed.....	1,112	838	24.7	19.11	19.30	19.30
	1,794	1,384	22.8	12.70	13.91	14.17
	127	58	1,827	902	50.6	18.50	18.80	18.80
	117	53	1,994	1,270	36.3	16.60	16.60	16.91
Average.....	123	56	1,750	1,186	31.7	15.95	16.49	16.68

Theory would lead to the conclusion that at about red heat the water of hydration is driven out of the sand-lime bricks, thus partly destroying the hydrated silicate bond. If high enough temperatures are reached, however, the recombination of the lime and silica might take place with the formation of an anhydrous calcium silicate bond, in which case a true silica brick would result. It was with the intention of testing this theory, and also of studying the effect of various degrees of heat on the strength of sand-lime bricks, that the experiment described below was carried out.

DESCRIPTION OF METHODS OF TESTING FIRE RESISTANCE.

MATERIALS USED IN TESTS.

The materials used in this experiment were two brands of commercial sand-lime bricks sent at our request by the manufacturer. There could have been no selection made at the factory other than the exclusion of

* Increase.

chipped or cracked specimens. More bricks were ordered than were actually required for the test, and only those free from cracks, checks, etc., were used.

APPARATUS USED IN TESTS.

The kiln used for burning is one belonging to the Department of Ceramics of the University of Illinois. It is of the down-draught type and has a capacity of 150 bricks. The first gases pass up the back, then down through the ware, up in front, and over the top to the flue. Connellsville coke was used for fuel, and temperatures were measured by the use of a thermo-electric couple of the platinum-rhodium type. The couple was enclosed in a quartz glass tube which was inserted into a fire clay tube set in the kiln. The crushing and cross-breaking strengths of the heated bricks were tested in two 100,000-pound Riehle testing machines belonging to the Laboratory of Applied Mechanics of the same University. These are exactly alike, except that on the slow speed, one advances at the rate of $1/5$ inch per minute, while the other is geared to move only half as fast. The latter of these was used for the transverse tests.

BURNING TESTS.

The procedure in burning was as follows: The bricks were set in the kiln, the fire-clay pyrometer tube was put in place, and a wicket was built up on the evening preceding the firing. The fire was started and about three or four hours were taken to bring the temperature up to 300° , when the first draw was made. The heat was then slowly increased and drawings of 11 bricks were made at each 100° rise in the temperature, until the maximum temperature was reached at the end of about 20 hours. When drawn, the bricks were allowed to cool, and were marked and carefully packed so as not to be injured in being removed to the laboratory where the tests were made. The burns at 1370° and 1290° were made at a later time in connection with some clay tests. The temperature was measured at this time by the use of Seger cones, Nos. 12 and 8 being the limits to which firing was carried.

TESTING.

The tests were made according to the latest specifications of the American Society for Testing Materials (Report of Committee at Atlantic City Meeting, July, 1909; published in Proceedings, Vol. IX.), which reads, in part, as follows:

"Transverse Test.—At least five bricks shall be tested, laid flatwise with a span of 7 inches, and with the load applied at middle span. The knife edges shall be slightly curved in the direction of their lengths. Steel bearing plates, about one-half inch thick and $1\frac{1}{2}$ inches wide, may be placed between the knife edges and the brick. The use of a wooden base-block, slightly rounded transversely across its top, upon which to

rest the lower knife edges, is recommended. The modulus of rupture shall be obtained by the following formula: $R = \frac{3We}{2bd^2}$ in which e is the

distance between supports in inches, b is the breadth and d the depth of the brick in inches, W is the load in pounds at which the brick failed.

"Compression Test.—Compression tests shall be made on half bricks resulting from the transverse tests. The bricks shall be bedded flatwise on blotting paper, heavy fibrous building paper, or felt, to secure a uniform bearing in the testing machine. * * * The machine used for compression tests shall be equipped with spherical bearing blocks. The breaking load shall be divided by the area in compression, and the results reported in pounds per square inch."

METHOD OF AVERAGING RESULTS.

The result of each individual test was recorded, but before taking their mean, one out of every eleven was discarded. The object was, of course, to eliminate any test that was noticeably out of accord with the others. In the case of the transverse tests there were several instances in which more than 10 per cent had to be discarded before taking the mean.

DISCUSSION OF RESULTS.

The results of the tests are shown graphically in figures 3 and 4, in which temperatures in hundreds of degrees centigrade are represented

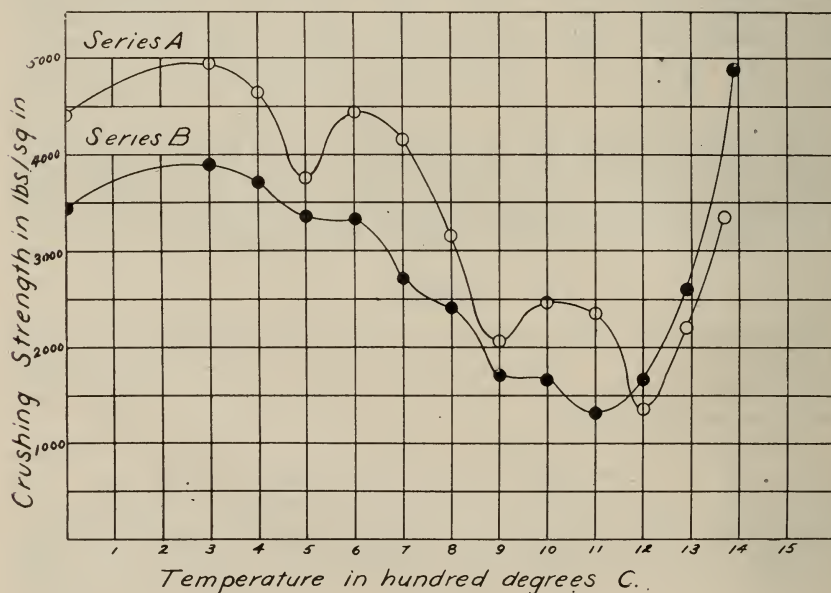


Fig. 3. Curves recording crushing strength of sand-lime bricks heated to different temperatures.

as abscissas, and pounds pressure as ordinates. The two curves in figure 3 show the reaction between crushing strength and temperature, and the two in figure 4 show the effect of heat on the modulus of rupture. It will be noticed that the modulus of rupture falls off continuously until 1100° is reached, and then begins to increase. The

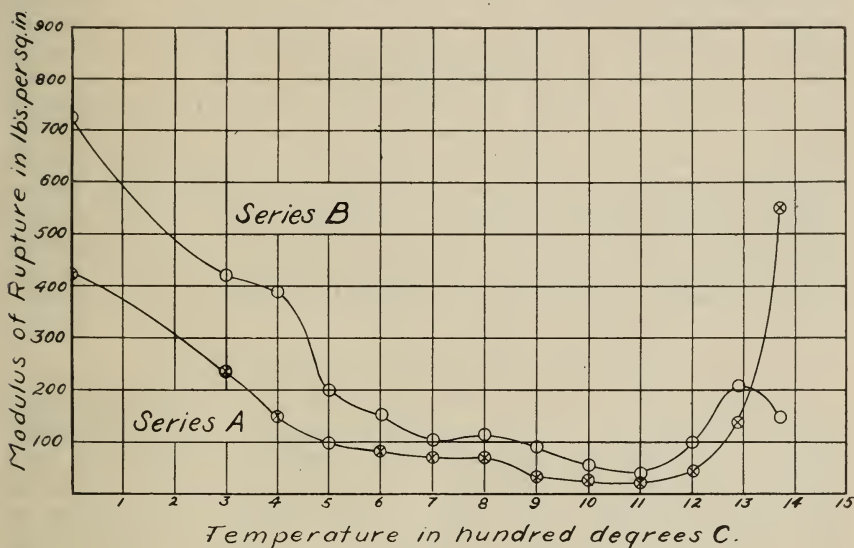


Fig. 4. Curves recording variations in modulus of rupture of sand-lime bricks heated to different temperatures.

curves recording compressive strength, on the other hand, show a marked increase at 300° . This can probably be explained on the supposition that at this temperature the bricks are more thoroughly dried than at lower temperatures, and that any combined lime originally present in them is changed to the carbonate by the fire gases. At 500° the curves have a minimum which has not as yet been satisfactorily explained. It is known,¹ however, that at 570° quartz undergoes quite a sudden change in volume, and this may explain the phenomenon.

The gradual fall in strength from 500° to 900° is probably brought about by a number of causes. First, after passing 600° water doubtless begins to come off quite rapidly; second, any calcium carbonate that has been formed will be decomposed between these limits; third, at 800° we have the point beyond which quartz ceases to be the stable form of silica and an inversion into tridymite begins. This inversion is accompanied by a marked increase in volume which is very detrimental to the bond. The final increase in both compression and transverse strengths is easily explained by the fact that here there is a combination of lime and silica to form a bond of anhydrous calcium silicate.

¹ Compt. Rendu. vol. 108, 1889, p. 1046 and vol. 109, 1889, p. 264. See also page 16 of this paper.

The results of the tests indicate that the compressive strength of sand-lime bricks will be diminished only slightly by any ordinary conflagration. Their transverse strength, however, diminishes at a rate very nearly proportional to the temperature, especially for low temperatures. It may be said in favor of sand-lime bricks, however, that in all the specimens tested there was not a sign of warping or shrinkage except at the highest temperature, where some of the samples cracked and warped badly. In nearly every instance of this kind there was found a lump of lime, in some cases of considerable size, which probably was the cause of the fracture. At 1200° the bricks had a very pleasing appearance, resembling very much a high grade buff face brick. In the tests for transverse strength the unburned bricks and those heated to the highest temperature broke with a snap; at all other temperatures the failure could be detected only by the drop in the scale beam. At the highest temperatures reached, and also at 500° in the case of one series, when subjected to the compression test the specimens failed with a crashing sound, resembling in this respect vitrified clay bricks.

CONCLUSIONS REGARDING FIRE RESISTANCE.

It has been shown that the effect of heat on the strength of sand-lime bricks is a function of the temperature reached. It is not probable that in an ordinary conflagration, the temperature often goes high enough to result in the formation of a true silica brick; so that in considering sand-lime bricks from the standpoint of their ability to pass with immunity through conflagrations only the first halves of the curves need to be considered. In any final conclusions as to the relative merits of sand-lime bricks as compared with other bricks, it must be remembered that strength is but one of many properties to be considered, and that in the matter of conductivity, shrinkage, coefficient of expansion, warping, etc., sand-lime bricks behave very well.

TABLE 30—*Fire tests on sand-lime bricks.*

Series A.			Series B.		
Temperature— Degrees C.	Modulus of rupture.	Compressive strength lbs. per square inch.	Temperature— Degrees C.	Modulus of rupture.	Compressive strength, lbs. per square inch.
000.....	430	4,382	000.....	717	3,430
300.....	238	4,980	300.....	418	3,900
400.....	145	4,650	400.....	388	3,710
500.....	95	3,720	500.....	197	3,340
600.....	83	4,440	600.....	142	3,320
700.....	68	4,155	700.....	100	2,640
800.....	68	3,130	800.....	116	2,400
900.....	33	2,050	900.....	85	1,700
1000.....	33	2,440	1000.....	61	1,680
1100.....	26	2,350	1100.....	37	1,280
1200.....	47	1,310	1200.....	101	1,670
1290.....	131	2,250	1290.....	210	2,505
1370.....	554	3,341	1370.....	157	4,560

SUMMARY.

In appearance, sand-lime bricks are very pleasing. Their color varies from a pure white to a dark gray. Where colored sands are used in mixtures from which they are made, brown, red and other colored bricks may be produced. The bricks may also be colored by an admixture of various kinds of coloring matter, or by precipitating coloring material within their pores. In cases where artificial coloring is to be practiced, it is essential that the sand used in making the bricks be of such a character as not to interfere with the color. It should, preferably, be fine and white.

Sand-lime bricks are very uniform in size and shape. They are larger than the ordinary clay bricks owing to the fact that they do not shrink on hardening, and therefore fewer are needed for the construction of a given mass of masonry. Again less mortar is required in laying the sand-lime bricks because of their regular shapes, and masons can work more rapidly with them because no time is required to select the best face for the outside of the wall.

From a careful consideration of all information at hand, the conclusion seems to be warranted that sand-lime bricks have successfully withstood every reasonable test required of them, and that the future of the industry in this country is assured. Replies received to circular letters sent out to the trade show that most manufacturers are prospering and that the prejudice always found to exist against a new building material is being gradually removed.

The future of the industry demands that a good, reliable product be put upon the market and at a reasonable price. In order that this may be done, it is essential that care be exercised in the location of manufacturing plants. The prospect of securing a ready market and of having at hand an abundant supply of good sand should weigh heavily in the final selection of a site.

The character of the sand should be taken into consideration in the selection of the process to be used in the preparation of the mixture of sand and lime. For the sake of economy in the use of lime, and in order to promote strength, and to reduce absorption in the finished bricks, the percentage of bonding material should not be very much in excess of that required to unite thoroughly the sand grains into one compact mass; or, in other words, should be just enough to fill the voids in a properly proportioned mixture of fine and coarse sands.

It has been shown that the bond of a sand-lime brick is a mixture of silicates of calcium, and that the simple calcium metasilicate or hydrometasilicate (CaSiO_3 or $\text{CaSiO}_3 \cdot \text{H}_2\text{O}$) is the principal compound of this mixture. Other silicates, as stated on page 59, must also be present in small, variable amounts, dependent on the conditions of manufacture of the bricks.

Sand-lime bricks have repeatedly passed satisfactorily all the tests recommended for building bricks by the American Society for Testing Materials. The effect of heat upon them has been shown to depend upon the temperature to which they are subjected, a red heat causing the bond to break up, while a white heat causes recombination. Enough work has been done along this line to warrant the statement that for all ordinary purposes sand-lime bricks afford a safe and reliable building material.

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